CONTRIBUTION TO THE THEORY OF PARACHOR

Jiří ČELEDA

Department of Nuclear Fuel Technology and Radiochemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6

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Dedicated to Professor S. Škramovský on the ocassion of his 80th birthday.

Deriving theoretically the dependence of the surface tension of a liquid substance, σ, on its density ϱ_l, the author has arrived by means of a simplified molecular-statistical model, to a temperature-independent product $\varrho_l^{-1}\sigma^{1/y}$, with denominator y in the exponent equal to $n/2 + 2/3$ (where n is the power of decrease of intermolecular potential energy of attractive forces, with increasing distance). Taking into account the finite gradient of the repulsive forces (exponent n'), we obtain an additional relatively small correction in a positive sense. The value resulting hence for y, in the case of the individual real compounds, is in average close to 4 — in agreement with the empirical formula of the Sugden parachor representing a temperature-invariant quantity. This quantity is subjected to theoretical analysis from the point of view of its applicability to investigation of the chemical constitution of substances in solutions, in terms of the additivity principle assumed by Sugden. As a result of this analysis, a concept is introduced of the apparent parachor of a solute, Π_i, (as a quantity experimentally accessible) — in analogy to its apparent volume Φ_i.

Additive quantities have always played important role in physical investigation of the chemical constitution of compounds, though their importance has receded as a result of development of modern methods for direct structure determination[1]. As a trivial example may serve the relative molecular mass M which is formed additively from the relative atomic masses representing individual atomic constants. A disadvantage of applying the molecular mass for the structural studies arises from the fact that within the limits of attainable accuracy, this parameter is sensitive neither to formation of the bonds between the atoms nor to the intermolecular forces. As a quantity which is most closely related to the molecular mass of the substance, can be considered its molal volume in the condensed state, M/ϱ. However, unlike the molecular mass, molal volume is sensitive to the above mentioned effects, exhibiting positive and negative deviations from the sum of the atomic increments which are taken as invariable constants at given temperature. The additivity of these increments — including constant corrections accounting for multiple bonds, cyclization of chains, *etc.* was studied for a very extensive set of 870 compounds by Exner[2]. The author found good agreement between, the values which were calculated (for the given structure of the substance) as the sum of the atomic and bond increments and, the experimental values of the molal volumes of substances in the liquid phase —under the condition that they were measured at one and the same temperature and pressure.

The applicability of quantity M/ϱ for the chemical structure studies is limited by the dependence of this quantity on temperature. One cannot compare molal volumes of those substances, for which the temperature or pressure ranges of existence of one and the same condensed phase are very different or which do not overlap at all. The density changes connected with these temperature or pressure differences enter, in such a case, into the structural increments and can lead to their erroneous interpretation. This fact is also evident from the above mentioned work of Exner[2] who noted that the molal volumes of liquid substances which were measured at one and the same temperature give a far better agreement for the additivity of the atomic volumes (including structural elements) than, *e.g.*, the volumes which were measured at boiling point temperatures of the same substances.

This uncertainty by which the above process of physical determination of the structure of substances is loaded can be eliminated by combining the experimental value of the molal volume with a suitable function of some other physical quantity depending on temperature in such a way that it can compensate the temperature changes of density ϱ. In this way, it is possible to determine the structural effects by comparing simply the data obtained at various temperatures. This is of course only true for such effects which give, for both the molal volume and the above compensating function, different relative changes. Most convenient seems to combine density ϱ with parameters which are, similarly to the density, a function of the number of particles in a volume element as, *e.g.* the refractive index (depending on the number of the electrons in a volume element), or, the relative permittivity or DC in the case of non-polar compounds. Applying the Clausius–Mosotti model of dielectric polarization, one thus obtains quantities which are invariant with temperature (specific refraction or specific polarizability[3] per 1 gram of substance). Multiplying these quantities by the molecular mass, we obtain molal characteristics which again consist of additive, temperature-independent structural and atomic contributions.

Surface tension σ, too, is a monotonous function of temperature which is able to compensate the temperature changes of the molal volumes of liquid substances, as long as these changes are monotonous as well. A temperature-invariant molal quantity which can be divided into additive atomic contributions (including the bond increments) is in this case, according to Sugden[4], defined by the formula $(M/\varrho_l)\,\sigma^{1/4}$. This product named by the author "parachor" P was derived from the empirical Macleod[5] temperature invariant $\sigma^{1/4}/(\varrho_l - \varrho_g)$, by the omission of density ϱ_g of the saturated vapour of a substance in question. This correction ϱ_g has been introduced by Macleod to account for the fact that at critical temperature (where $\varrho_l = \varrho_g$), the surface tension of each liquid phase falls in contact with its saturated vapour to zero.

If we assumed that surface tension (representing the energy in a unit surface area) is proportional only to the coverage of the surface with molecules of a liquid, we would get a temperature independent expression $\sigma(M/\varrho_l)^{2/3}$. However, long time before the cited authors, Eötvös[6] recognized that the above product depended on temperature and he succeeded to describe this dependence empirically for experimental data of a selected set of compounds. He applied a two-parameter linear function of the difference $(T_c - T)$, using identical parameters for the whole studied system (T_c is the critical temperature of a substance). Validity of the Eötvös equation was tested experimentally, for a large selection of substances of various types, again by Exner[7]. Among others, Exner observed that for selected constant temperature, the Eötvös parameters gave a good fit only for small, roughly spherical molecules — up to pentanes for alkanes and up to toluen with aromatic hydrocarbons.

Another theoretical approach is based on a solution of the van der Waals equation of real compounds, for the region of coexistence of the gaseous and liquid phase. In this way it has been possible to derive[8] that the expression $M(\varrho_l - \varrho_g)^{-1}\,\sigma^{1/y}$ should be independent of temperature for the denominator value of the exponent $y = 3$. This value is visibly lower than the numbers given by Sugden[4], Macleod[5] and Bachinskij[8], $y = 4$. So far, all theoretical explanations for the above (or near) values have led to the recognition that this value was somehow incorporated into the intial relations either in the form of the arbitrary premisses or as a consequence of the empirically observed relations among other quantities. As an example, one can mention the derivation given by Eucken[9], who, combining the empirical state equation of liquids with the London cohesion theory, obtained a temperature independent expression $\sigma^{3/11} \varrho_l^{-1}$ — which corresponds to the value $y = 11/3$, close to the number given by Sugden, $y = 4$.

Sugden's invariant with the value $y = 4$ was critically tested again by Exner[10] on a large group of over 400 liquid substances. The author used a special, own statistical procedure which eliminated the contribution introduced into the results by the additivity of the molal volumes (eventually by the additivity of the atomic masses themselves). Exner proved that Sugden's expression with $y = 4$, in general, does not fulfil even the condition of the temperature invariability, with the exception of the group of non-polar and slightly polar compounds of not very complicated molecular structure. In addition to this the above expression also does not fulfil the condition of the additivity of atomic and structural increments or the last one only with the accuracy about one order of magnitude lower than with the molal volumes of the substances measured at one and the same temperature.

Under these circumstances where we had, thanks to the above cited papers, at our disposal a rich experimental material on the correlations but practically no relevant theoretical basis, we have set the aim of the present paper in theoretical solution of the following questions:

1) is it possible to find a physically substantiated model which would permit to derive the functional dependence of the surface tension of liquid substances on their density ϱ_l at various temperatures? If so, will this dependence have a character of a power function and what will be the value of its exponent?

2) in a case that such a function can be found, is it possible to explain, on physical basis, the additive behaviour of its temperature-invariant ratio to ϱ_l, also for the liquid mixtures and for the solutions of solid substances? This could be important for the experimental determination of this characteristic of individual substances, from the data measured on their solutions, in the temperature range where the compound itself cannot exist in a liquid state; such a case is typically found with aqueous solutions of inorganic salts[11] especially then if we want to study their complexes or associated forms which do not exist in a molten state.

THEORETICAL

Parachor as a Temperature-invariant Quantity

For a solution of the above problem, we used a drastically simplified model of surface tension. The author of the present work arrived to this model as a result of his attempts to find a direct way of applying the surface tension of aqueous electrolyte solutions for detection of the formation of complexes in solutions[12]. In this model, the surface tension of the liquid is calculated as a work required for reversible and isothermal formation of a unit surface area of the liquid. In the given model representation, we can imagine that this process proceeds by a reversible splitting of a liquid column of diammeter Q, accompanied by simultaneous formation of two new surfaces with total area $2Q$. Both surfaces are in equilibrium with the saturated vapour of the substance at given temperature. This means that all particles on one side of the boundary have to be separated from all particles in the opposite layer. The work defined in this way is equal to the product of the number of particles in the overall are of the surface layer $Q/\bar{r}_l^2$ (where $\bar{r}_l$ is the mean effective distance of the particles in a liquid) and, the work w_σ connected with separation of a single particle from all particles in the opposite layer.

For rough orientation, work w_σ can be at temperatures deep below T_c simply correlated with the heats of vaporization at these temperatures, L, (since under these conditions, the volume work contribution and the entropic term in σ are unimportant):

$$w_\sigma = L/(N_0 p) \,. \tag{1}$$

In the above expression, N_0 is the Avogadro constant and coefficient p represents a quotient of, the work required for removal of one particle in the course of evaporation out of the bulk of the liquid and, the work needed for separation of this particle from the opposite layer. This quotient includes also a correction for the interactions with the layers located more deeply. Its numerical value depends on the molecular structure of the given liquid and, as follows from the definition, its value should lie in the range of units. For non-polar compounds bound by short-range forces of prevailingly dispersive character (for which the attractive interactions are additive[13]), the value of this coefficient should be close to one half of the coordination number N_c of the molecules in the liquid, since after separation of one particle from the association with its N_c neighbours, N_c interaction centers are freed which can restore $1/2\, N_c$ short-range cohesive interactions between the remaining molecules. For the surface tension, we thus get a relation

$$\sigma = w_\sigma(Q/\bar{r}_l^2)\,(2Q)^{-1} = \tfrac{1}{2} w_\sigma \bar{r}_l^{-2} \,, \tag{2}$$

where, in the same approximation, $\bar{r}_l$ can be expressed as the function of density ϱ_l of a liquid, from equation

$$\varrho_l = (M/N_0)\, \bar{r}_l^{-3} \,. \tag{3}$$

Substituting (1) for w_σ, we obtain from (2), for the product $p\sigma$, the expression $[\tfrac{1}{2}L/ /(N_0 p)]\, \varrho_l(N_0/M)^{2/3}$. In this expression we can (because of the very rough approximations introduced into the model) express further the vaporization heats, L, with the standard boiling points T_b. Using the thermodynamically justified value[14] $L/T_b = 90\ \mathrm{J\,K^{-1}\,mol^{-1}}$, we obtain after evaluation of the constants

$$p\sigma = 5{\cdot}4 \,.\, 10^{-7}\, T_b(\varrho_l/M)^{2/3} \tag{4}$$

where the molal volume of the substance is expressed in $\mathrm{cm}^3\,\mathrm{mol}^{-1}$ and the surface tension σ in $\mathrm{J\,cm}^{-2}$ ($= 10^2\,\mathrm{N\,cm}^{-1}$ *i.e.* $10^7\,\mathrm{dyn\,cm}^{-1}$).

It may be expected that the association effect in strong polar liquids is in this way partially compensated. This effect increases the effective molecular mass of the particles moving at the standard boiling point temperature from the liquid to the vapour phase but it also simultaneously increases the value of the Trouton ratio L/T_b (ref.[14]). On the other hand, this step inserts in the calculation a restriction which disagrees with physical reality. The vaporization heat L of a substance decreases with rising temperature while the standard boiling point T_b is for each compound a characteristic strictly defined constant. By substituting heat L with a constant multiple of T_b, one eliminates the temperature dependence of the vaporization heat from equation (*4*). This equation, therefore, does not give any more a correct description of the dependence of the surface tension of a liquid on its density, at varying temperature, and it cannot be thus applied for such purpose. As a matter of fact, Trouton's rule holds exactly only for the vaporization heats of liquids at their standard boiling point temperatures. Equation (*4*) thus provides for coefficient p true values only when it is applied with the surface tension σ and density ϱ_l values which these liquid substances have at their standard boiling points, or because for the partial compensation of the differences in σ and ϱ_l, which were at least obtained at temperatures relatively not very far (expressed in the absolute Kelvin scale) from their boiling points. For compounds which exist at normal temperatures as liquids, it is possible in rough approximation to use their surface tension at ambient temperatures 15–20°C. However, for compounds with very high boiling points, one has to use values obtained at comparably high temperature.

The described formulation of the model and the hence derived basic energy relations accessible to experimental tests enabled us to calculate a relation between the surface tension of a substance (representing the work required for mutual separation of its particles) and its density (related to mean distance of its particles). For this purpose, the model was complemented by the assumption according to which every particle in the liquid exhibits, in the field of each of its adjacent particles, vibrations in a potential well. This well is limited in the direction towards the neighboring particle by a barrier given by the repulsive forces by which the particle possessing total energy E_L is stopped at the distance r'_L. In the direction "outwords", the boundary of the well is determined by the potential curve of the attractive forces and the particle collides with it at the distance r_L. With rising temperature, the vibrating particles fill up higher and higher quantum states, in accordance with the corresponding partition function, and mean energy of the particles E_L (measured from the "bottom" of the potential well taken, in the model, as the intersection point of both curves), continuously increases. As a result, energy E_σ (connected with full separation from the adjacent molecule and determining the surface tension) goes down while the mean distance between the particles $\bar{r}_l$ (determining the density of the liquid) simultaneously goes up.

We have calculated this mean distance, using the above model, by integration along the range of one full vibration, from r'_L to r_L. The energy corresponding to the repulsive and attractive forces can be written in the form of a power function of the distance r between the particles:

$$-E_{rep} = A_{rep}r^{-n'} = (r/n')\,dE_{rep}/dr \tag{5}$$

$$-E_{att} = A_{att}r^{-n} = (r/n)\,dE_{att}/dr\,. \tag{6}$$

In the first case, the energy is changing with increasing r by 3 to 6 orders of magnitude[15] faster than in the second case. For $r > r_0$ (where r_0 corresponds to the bottom of a potential well) one can, therefore, in approximated representation omit the repulsive term in potential energy E_{pot}. At normal temperatures, where energy E_L belonging to the perpendicular degree of freedom is for most liquids by one or more orders of magnitude lower than the separation work w_σ, the amplitudes $r_L - r_0$ and $r'_L - r_0$ are very small compared to r_0 and the potential energy curve of the particle in the field of attractive forces of its neighbour can be for the whole range substituted by a straight line. The slope of this line is identical with the value obtained for the gradient of E_{att} from (*6*) (for $r = r_0$), *i.e.* nw^0_σ/r_0. We have taken for the mean value of $-E_{att}$, in this range, the separation work w^0_σ which is required to overcome at $r = r_0$ the attractive force alone.

The barrier of the repulsive forces which steeply increases at $r < r_0$ can be in rough approximation replaced by a vertical wall on which the particles rebound; in such a case $n' = \infty$ and $r'_L = r_0$. If we respect the finite value of the gradient of E_{rep}, it is satisfactory to substitute curve E_{rep} (since in terms of the present model we deal with a less important correction) – in analogy to the case of E_{att} – with a function linearly dependent on r, with a tangent increased $(n'/n)^{k+1}$ times. In this representation, parameter k depends on a mutual ratio of the constants A_{rep} and A_{att} (respectively energies E_L and E_σ $(= -w_\sigma)$) and, for $E_L \ll E_\sigma$, we obtain for this parameter under normal circumstances nearly in all cases values larger than 1. For the "lower" amplitude of r'_L, we get then the value $r_0[1 - (n/n')^k\, E_L/(n'w^0_\sigma)]$.

Calculating the mean distance of the particles, $\bar{r}_l$, for a range from r'_L to r_L, one has to consider the corresponding statistical weights for the individual distances r. These weights are proportional to the stay-time of the particle in each interval dr during the vibration, *i.e.* to dr/v (where v is the instantaneous velocity of the particle given by a relation):

$$v = [2(E_L - E_{pot})/m]^{1/2}\,. \tag{7}$$

There, m denotes the mass of a particle and the difference $E_L - E_{pot}$ in its kinetic energy E_{kin} at a particular place. Applying the usual averaging formula and integrating from r'_L to r_0 and hence from r_0 to r_L, we obtain after eliminating the constant coefficients and back-substitution of the preceding expressions:

$$\bar{r} = r_0 + \tfrac{2}{3}[1 - (n/n')^{k+1}]\,(r_L - r_0)\,, \tag{8}$$

where k is a variable parameter, depending on mutual relation between the repulsive and attractive forces in the given temperature range. Considering that the total energy of a particle E_L is in the present model related, according to (*6*), to the amplitude r_L by the equation of the "outer wall" of a potential well

$$\mathrm{d}E_L/\mathrm{d}r_L = n\, w_\sigma^0/r_0 \tag{9}$$

and since the relative volume dilatation coefficient $-(\mathrm{d}\varrho_l/\varrho_l)/\mathrm{d}T$ is equal to a threefold multiple of the linear dilatation coefficient, we get

$$-\mathrm{d}\varrho_l/\varrho_l = 3\mathrm{d}\bar{r}_l/\bar{r}_l \tag{10}$$

and from (*8*) to (*10*) we obtain the dependence of the energy E_L on density ϱ_l:

$$\mathrm{d}E_L/\mathrm{d}\varrho_l = -\tfrac{1}{2}n[1 - (n/n')^{k+1}]^{-1}\, w_\sigma/\varrho_l\,. \tag{11}$$

The quotient w_σ^0/r_0 was substituted (due to the relatively small difference in $\bar{r}_l - r_0$ compared to r_0) with a ratio $w_\sigma/\bar{r}_l$ where, as before, w_σ signifies the separation work of a molecule at the given energy level $E = E_L$.

Since the temperature increase of the total energy of a particle E_L, in the force field of the opposite layer is equal (within previously mentioned limitations) to the decrease of its reversible separation work w_σ from this layer, we can substitute in equation (*11*), $-\mathrm{d}w_\sigma$ for $\mathrm{d}E$, and in this way we obtain the required dependence of the separation energy on density ϱ_l:

$$\mathrm{d}w_\sigma/w_\sigma = \tfrac{1}{2}n[1 - (n/n')^{k+1}]^{-1}\, \mathrm{d}\varrho_l/\varrho_l\,. \tag{12}$$

This expression is valid for one given substance for different temperatures. From equations (*2*), (*3*), (*10*) and (*12*), we can then easily find the dependence of the surface tension of a liquid substance on its density:

$$\mathrm{d}\sigma/\sigma = \mathrm{d}w_\sigma/w_\sigma - 2r_l^{-1}\,\mathrm{d}r_l = (\tfrac{2}{3} + \tfrac{1}{2}n[1 - (n/n')^{k+1}])\,\mathrm{d}\varrho_l/\varrho_l\,, \tag{13}$$

which can be written as

$$\mathrm{d}\ln\sigma = y\,\mathrm{d}\ln\varrho_l \tag{14}$$

or

$$d \ln (\sigma^{1/y}/\varrho_1) = 0 , \qquad (15)$$

where

$$y = \tfrac{2}{3} + \tfrac{1}{2}n[1 - (n/n')^{k+1}]^{-1} . \qquad (16)$$

Virial exponents n and n' are given by the specific physical properties of the molecules (in the first place polarity of the bonds[15,16]) which can change from substance to substance. Hence follows

$$\sigma^{1/y}/\varrho_1 = \text{const.} \qquad (17)$$

for a temperature invariant quantity which after multiplication by the molecular mass M gives a molal temperature invariant for liquid compounds

$$P = M\sigma^{1/y}/\varrho_1 \qquad (18)$$

which is in fact the Sugden parachor, yet, with a variable exponent $1/y$.

Accuracy of the above result can be further improved by considering the fact that the molecules on a new surface formed by a reversible isothermal splitting of the column are not in contact with the vacuum but that they face a volume filled with saturated vapour. In the most simple (of course very rough) approximation we can imagine that all collisions of the vapour molecules with the surface molecules are simply subtracted from the number of the molecules in a liquid as if each molecule of the vapour has saturated the valence forces of the adjacent molecule in the surface layer, eliminating it thus from the energy balance in the separation process. The number of particles in the liquid contributing to the separation work of formation of the new surface is, thence, relatively decreased in proportion to $1 - \varrho_g/\varrho_l$. By multiplying the density of a liquid in expression (*18*) by this correction coefficient, one is replacing density ϱ_l with a difference $\varrho_l - \varrho_g$ – in correspondence with the formulation of Macleod which is therefore from the physical point of view more exact. Nonetheless, since $1/y < 1$, from (*18*) it is qualitatively evident that Sugden's omission of the correction on ϱ_g is acceptable up to temperatures close to T_c.

The first term in equation (*16*) is "eötvösian" and it tranforms the dilatation decrease of the volume concentration of particles (which is proportional to $1/r_l^3$) to the decrease of surface concentration which is a quantity proportional to $1/r_l^2$. The second term respects the fact that the decrease of surface tension observed for decreasing density ϱ_l is caused not only by the dilution of the particles in the surface of the separation plane (as described by equation (*4*)) but that with increasing mean distance $\bar{r}_l$ decreases also the cohesion energy of the particles. The latter effect is far more significant than the former one.

Additivity of the Parachors in Mixtures

Solving the above problem, we have started with a model of the ideal liquid mixture for which it holds that its volume is equal to the sum of the volumes which the components would have in their pure states. In such a case, the density of this mixture $\varrho_l = \overline{M}/V$ is equal to $\overline{M}/\sum x_i M_i \varrho_i^{-1}$ (where $\overline{M}$ is the mean molecular mass of a mixture, x_i are the molar fractions of components and ϱ_i are the densities of these components in their pure liquid states). The surface tension can be for this case expressed by means of the Guggenheim coverage model[17] according to which to each component in the boundary layer corresponds an amount which is equal to its volume fraction in the mixture $p_i = (x_i M_i \varrho_i^{-1})/(\overline{M}\varrho^{-1})$. Each of the i components borders on all j components in the opposite layer, in proportion to their volume fraction, with separation energies $w_{i,j}$. If we assume, in analogy with the previous work[12] for $w_{i,j}$, a value $\frac{1}{2}(w_{ii} + w_{jj})$, we obtain for the surface tension of a mixture σ, the value $\sum p_i \sigma_i$.

Such ideal mixture can be formed only by non-polar compounds, consisting of rigid spherical molecules, bond by dispersion forces without a pronounced directional character. This corresponds, at the same time, to very high values of the repulsion exponent n' ("hard-sphere model") while all attraction exponents n are in this case, for all components, at their highest possible value n_0. Parachor y calculated from equation (*16*) is then for all components practically identical. (If not so, we could have no physical justification for adding the parachors of the individual components since these would be quantities with different dimensions). For the parachor of the overall mixture

$$P = (\overline{M}/\varrho)\,\sigma^{1/y} \tag{19}$$

we thus obtain a formula $\sigma^{1/y} \sum x_i M_i/\varrho_i$ in which it is possible to express the fractions M_i/ϱ_i of the individual components (using their pure state parachors for the same temperature) as quotients $P_i/\sigma_i^{1/y}$, with a common value y. Expressions $x_i P_i(\sigma/\sigma_i)^{1/y}$ resulting from all terms of the above sum can be further rewritten in the form $x_i P_i[1 + (\sigma - \sigma_i)/\sigma_i]^{1/y}$. Because of the low value of the exponent y, the powers of the binomials can be in approximation further substituted with expressions $1 + (\sigma - \sigma_i)/(y\sigma_i)$. The polynomial obtained for the parachor of the mixture is in this way splitted in two parts:

$$P = x_i P_i + \frac{1}{y} \sum x_i M_i \varrho_i^{-1} \sigma_i^{(1/y)-1} (\sigma - \sigma_i)\,. \tag{20}$$

In this expression, the latter term represents the correction term ΔP. Dividing this difference by the value of P, according to (*19*), we obtain for the relative correction of the parachor of a solution

$$\Delta P/P \approx (y\sigma)^{-1}\,(\sigma/\bar{\sigma})^{1-1/y}\,(\sigma \sum p_i - \sum p_i \sigma_i)\,. \tag{21}$$

As before, we have substituted back into this expression the surface fractions of the components p_i and introduced quantity $\bar{\sigma}$ for the mean value of surface tension of the components in the exponential factor in (*20*) which was averaged on the level of their $(1 - 1/y)$th powers.

Considering that according to the Guggenheim model of the surface tension for ideal mixtures, the second term in parentheses in equation (*21*) is equal to the surface tension of the mixture, σ, and taking into account that $\sum p_i = 1$, we get for the binomial in parentheses on the right-hand side of equation (*21*), the value of zero so that the whole correction term becomes nil. In this way we have substantiated the additivity of the parachors of the components assumed by Sugden and others

$$P = \sum x_i P_i \tag{22}$$

nonetheless, only with a precision corresponding to the applied approximations (use of a common value for y, replacement of all σ_i in the product with a common mean value $\bar{\sigma}$ and finally substitution of the $1/y$-th powers in the binomials $(1 + \delta)$ with linearized expressions $1 + \delta/y$).

In non-ideal mixtures, the additivity does not hold exactly even for the case of the molal volumes. For treating this problem numerically, it was useful to formulate for the solutions the notion of the "apparent" molal volume of a solute Φ_1, as the volume which is left per one mole of the solute after subtraction of the whole volume of the solvent, taken as a pure substance in liquid state at given temperature (with density ϱ_0 and molal volume $V_0 = M_0/\varrho_0$). From this definition we get for the apparent molal volume of the solute, the expresion

$$\Phi_1 = (1/x_1)(\bar{M}/\varrho - x_0 M_0/\varrho_0), \tag{23}$$

where ϱ denotes the density of the solution, $\bar{M} = x_0 M_0 + x_i M_i$ is its mean molecular mass and indices 0 and 1 relate to the solvent and solute respectively.

Using transformation of the molar fractions x_i to mass percents of the components q_i (calculated from their known weights in the experiments) which is independent of the degree of ideality of the solution:

$$x_i = (q_i/M_i)/(100/\bar{M}) = (q_i/100)\,\bar{M}/M_i \tag{24}$$

we can rewrite (*23*) to a form

$$\Phi_1 = (M_1/q_1)\left[(100/\varrho) - (100 - q_1)/\varrho_0\right]. \tag{25}$$

It is evident from this expression that for the known w/w percentage of the dissolved substance, q_1, one does not need to know, for the calculation of its apparent volume from the experimental density of the solution, the molecular mass of the solvent since the last cancelled out in the transformation process. This means that the evaluation of the apparent volume of a solute from the experimental densities of its solutions is independent of its solvation, as well as, of the association or polymerization of the solvent, *etc.* An analogous step from the ideal to real solutions can be carried out, based on equation (*22*), also for the parachors of the dissolved substances, *i.e.* one can formulate a notion of the "apparent parachor" of a solute, Π_1, representing the parachor remainder obtained per 1 mol of the solute after subtracting from the parachor of the solution as a whole, the parachor of the whole solvent, taken as pure liquid compound at the same temperature:

$$\Pi_1 = (1/x_1)\left(\sigma^{1/y}\overline{M}/\varrho - x_0\sigma_0^{1/y}M_0/\varrho_0\right). \qquad (26)$$

There, σ and σ_0 denote the surface tension of the solution and of the pure solvent at given temperature. Converting again the molar fractions into the w/w percents according to (*24*), we arrive to the formula for evaluation of the apparent parachors from the experimental data (the density of a solution and its surface tension)

$$\Pi_1 = (M_1/q_1)\left[(100\sigma^{1/y}/\varrho) - \sigma_0^{1/y}(100 - q_1)/\varrho_0\right]. \qquad (27)$$

This expression, too, is independent of our knowledge of the molecular mass of the solvent and, consequently, of its association or its depolymerization due to solvation of the solute, as well as, of the solvation degree of the solute itself. The quantity defined in this way includes all deviations from the additivity of the parachors of the components expressed by equation (*22*) whether they originate from the non--additivity of the molal volumes of the components or from approximations introduced when deriving this equation (the Guggenheim coverage model, linearization of the y-th root, *etc.*)

RESULTS AND DISCUSSION

Relation Between the Surface Tension of the Substances and Their Boiling Points

In order to test the basic applicability of the initial model of surface tension, we can apply with advantage equation (*4*) expressing on basis of this model, the theoretical relation between the surface tension of the liquid substance at absolute temperature T not very distant from its standard boiling point (which means for most organic compounds, at room temperature) and this standard boiling point T_b. Because it is not easy to select from the enormous supply of available data a suitable set which would characterize the broad variability of the various types of substances, we have let our choice to chance, including in our testing compounds for which the experimental data on σ, ϱ_l and T_b (ot t_b) were accessible in current handbook tables[18–20] and university level textbooks of physical chemistry[21–22]. The obtained results are summarized in Table I.

In spite of the fact that this random selection includes substances of very different types, the values obtained for parameter p (evaluated on basis of equation (*4*)) are nearly in all cases close to number 3. According to the model used, this corresponds to the coordination number 6. Higher values are obtained for strongly associated polar liquids (alcohols, organic acids *etc.*), yet, even in such cases the value of p remains within the range of units. It is worth to note that similar values for parameter p are noticed also with the molten metals, notwithstanding the fact that their surface tensions, temperatures T_b and densities are by one order of magnitude higher than in the above cases. An anomaly is found with mercury for which the separation surface work is close to the work required for complete removal of an atom from the bond of all its neighbours which corresponds to the coordination number slightly higher than 2. Relatively low – compared with other strongly associated polar compounds – is also the value of parameter p in the case of water. This can be caused by its relatively low coordination number in the liquid state which can be, as a result of formation of rigid hydrogen bonds, close to 4.

The high values of parameter p observed in molten salts are evidently related to the far-going association in their vapours. Particles escaping from the fused salt at temperature of the standard boiling point are seldom free ion pairs (for which the calculated values of p are shown in Table I) or even free monomer ions, but – as a rule – larger aggregates (lattice clusters). Cubic particles consisting of 8 ions – four ion pairs – (which can leave the liquid phase, as far as free energy is concerned, relatively more easily than the monomer ion pairs or – on the other side – bigger clusters) give, after substitution of tetrameric molecular masses M, for p the following values: 4·0 for NaBr, 4·2 for NaCl, 3·6 for AgCl and 2·7 for NaF or, in general, the same values as found for the low-boiling compounds with surface tension about ten times lower or for metals with surface tension about ten times higher. The fact that equation (*4*) is able to yield reasonable results in a surface tension range of two orders of magnitude can serve as an argument in favour of the applied model of surface tension σ.

Exponent $1/y$ in the Formula of the Parachor as a Temperature-independent Quantity

Equation (*16*) derived from the described model shows that the exponent in the formula of the parachor, representing a temperature-invariant quantity, is a function of the virial exponents of intermolecular repulsion and attraction energies. The theory of van der Waals forces[15,16,23,24] for non-polar and weakly polar substances gives for exponent n a value $n = 6$ while for the exponent n', both the theoretical considerations and experimental data lead[15] to values close to 12. In the case of

TABLE I

Parameter p in equation (*4*) evaluated from the experimental surface tensions of liquid substances σ and their densities ϱ_l at ambient temperature and from their standard boiling points T_b

Substance	σ 10^{-7} J cm^{-2}	ϱ_l g cm^{-3}	T_b K	$p\sigma$ 10^{-7} J cm^{-2}	p
$(C_2H_5)_2O$	17	0·72	308	75	4·4
n-C_6H_{14}	18	0·66	342	72	3·9
n-C_3H_7OH	21	0·81	370	113	5·3
C_2H_5SH	22	0·85	310	96	4·4
C_2H_5OH	22	0·79	352	127	5·8
CH_3OH	23	0·79	338	154	6·8
i-C_4H_9OH	23	0·80	381	101	4·4
CH_3—CO—CH_3	23	0·79	329	102	4·4
i-$C_5H_{11}OH$	24	0·81	405	96	4·0
CH_3COO—C_2H_5	24	0·90	350	84	3·5
CH_3COO-(i-C_5H_{11})	24	0·87	414	80	3·3
C_6H_5COO-(n-C_5H_{11})	24	1·01	533	87	3·6
CH_3COO—CH_3	24	0·92	330	96	4·0
C_2H_5Br	24	1·46	311	95	3·9
cyclohexane	25	0·78	354	84	3·3
CCl_4	26	1·59	350	90	3·5
$CHCl_3$	27	1·49	334	97	3·7
CH_3COOH	28	1·05	391	142	5·1
C_6H_5—CH_3	28	0·87	384	92	3·3
C_6H_6	30	0·88	353	90	3·0
m-$C_6H_4(CH_3)_2$	30	0·86	412	91	3·0
C_2H_5I	30	1·94	346	101	3·4
C_6H_5Cl	34	1·11	405	100	3·0
CS_2	34	1·27	319	112	3·3
C_6H_5COO—C_2H_5	35	1·06	486	97	2·8
C_5H_5N	37	0·98	389	113	3·1
HCOOH	38	1·23	374	180	4·8
C_6H_5OH	41	1·08	455	125	3·1
$C_6H_5NH_2$	42	1·02	458	122	2·9
$C_6H_5NO_2$	43	1·20	484	120	2·8
C_9H_7N	44	1·10	511	114	2·6
Br_2	44	3·14	332	131	3·0
CH_2I_2	51	3·33	454	131	2·6
$CHBr_3$	51	2·89	424	115	2·3
$C_3H_5(OH)_3$	63	1·26	563	174	2·8
D_2O	68	1·11	375	293	4·3
H_2O	73	1·00	373	293	4·0
NaBr (1 000°C)	88	3·1	1 660	888	10·1
NaCl (1 000°C)	98	2·1	1 740	1 043	10·6
AgCl (450°C)	126	5·5	1 830	1 133	9·0

TABLE I
(*Continued*)

Substance	σ 10^{-7} J cm^{-2}	ϱ_l g cm^{-3}	T_b K	$p\sigma$ 10^{-7} J cm^{-2}	p
NaF (1 010°C)	260	2·7	1 980	1 750	6·7
Hg (0°C)	470	13·6	630	570	1·2
Ag (970°C)	800	10·4	2 220	2 780	3·5
Au (1 070°C)	1 000	19·0	3 230	3 700	3·6
Cu (1 130°C)	1 100	8·8	2 870	4 100	3·7

strongly polarized substances with deformable molecules, this number tends to be lower, down to 9. Accepting, for low-polar substances, the values $n = 6$ and $n' = 12$, we find from (*16*), for y (for the limits from $k = \infty$ (hard-sphere model) to $k = 1$ (the lowest arbitrary limit)), values from 3·67 to 4·67. This is in good agreement with the limits from 3·1 to 4·8 given by Desreux[25] on basis of the experimental data. It should be noted that the lower limit 3·1 given by Desreux extends partially over the region of more polar compounds which the above author also included in his considerations. In the paper of Exner[10], one can find in the case of polar compounds, for the lower limit of y, even a value close to 2.

It can be easily derived theoretically that the value of the exponent n should go down with increasing polarity of the substance. Thus for molecular dipoles in the state of full mutual orientation, one gets $n = 3$, while for dipoles of large dimensions Lifshits[26] derived a value as low as 2, which is however valid only for particles approaching macroscopic sizes. Taking for polar compounds, for the lower limits, values $n = 3$ and $n' = 9$, we get from (*16*) (with k from ∞ to $k = 1$) for the lower limit of y 2·17 to 2·00 – in accordance with the values found for this type of substances by Desreux and Exner.

The values of the exponent-denominator y have been determined recently, for a variety of non-polar up to strongly polar compounds, in a non-standardized way by Svoboda and Charvátová[27]. The authors included into their calculation of y, the density of saturated vapour, ϱ_g, according to the original formulation of Macleod[5], using sophisticated elimination of the necessity to know direct experimental values for ϱ_g in the whole investigated temperature range up to the proximity of T_c. The difference between the density of the liquid and its saturated vapour which is required for the evaluation of the Macleod invariant in its general form $\sigma^{1/y}/(\varrho_l - \varrho_g) = \text{const.}$ was expressed by the authors as an integral from the Clapeyron equation for the heats of vaporization. In this way, they obtained a relation between the temperature dependence of the surface tension of a substance and the temperature dependence of the vaporization heat of the same substance, where the exponent $1/y$ appears directly in the equation. Using this equation and the experimental data on density, surface tension and vaporization heats of the liquids, the authors evaluated parameter y for a selected set of compounds with different degree of polarity. The results obtained for y are confronted in Table II with the dipole moments μ and permittivities ε of the studied compounds. Table II also shows the values of the exponent n evaluated according to (*16*), using a typical value of the difference $n' - n = 6$ and the limits from $k = 1$ to $k = \infty$ (hard-sphere model). The decrease of the value of parameter y towards the theoretically derived lower limit $y = 2$, with increasing polarity, is evident. The hence evaluated exponents of intermolecular cohesion energy, n, approach, when proceeding from non-polar to polar substances, the lower limit $n = 3$ which is a value true for mutually oriented dipoles.

Parachor and the Structure

According to the model used, surface tension of the liquid compounds should be predominantly determined by the intermolecular forces. Intramolecular bond relations should interfere only indirectly – to the extent in which they affect the intermolecular forces. One can, for example, expect that the presence of the multiple bonds and conjugated systems in the molecule will increase the surface tension as a result of the increased polarizability of the molecules which increases their separation work w_σ. Unlike this indirect influence on surface tension, in the case of the mola volumes, the intramolecular bond relations play a direct role; the multiple and con-

TABLE II

Dimensionless parameter y of liquid substances (exper.[27] from $\Delta H_{\text{evap.}}$) and the exponent of cohesion energy n in Eq. (*16*) calculated from y

Substance	μ aC pm	ε (relat.)	y	$n(k = \infty)$	$n(k = 1)$
$C_3H_6(CH_3)_2$	0	1·9	3·46	5·6	4·5
n-C_5H_{12}	0	1·8	3·23	5·1	4·2
n-C_6H_{14}	0	1·8	3·23	5·1	4·2
n-C_7H_{16}	0	1·9	3·23	5·1	4·2
n-C_8H_{18}	0	1·9	2·99	4·6	3·9
C_6H_6	0	2·3	2·99	4·6	3·9
CCl_4	0	2·2	2·99	4·6	3·9
$(C_2H_5)_2O$	3·5	4·2	2·96	4·5	3·9
C_2H_5SH	3·0	(8)	2·39	3·4	3·1
n-C_3H_7OH	5·6	22	2·47	3·6	3·2
C_2H_5OH	5·6	25	2·22	3·1	2·8

jugated bonds lead to shortening of the interatomic distances and in this way they increase considerably also the density of the liquid. This interaction acts in the same direction as that in the surface tension but the magnitude of this effect can be much larger, especially when it is confronted with the power of the surface tension lower than 1, as it is in the case of the parachor. On basis of the model used, one can therefore theoretically expect that the specific structural features of the substances will appear in the parachor as effects acting in the same direction as in the molal volumes but with the corresponding increments diminished as a result of partial compensation by the parallel changes of the surface tension.

The experimental data fully support the above conclusion. This can be visualized by a simple comparison of the compounds of similar composition but with different types of bonds; so, *e.g.*, in the sequence n-hexane–cyclohexane–benzene for which the density is changing in a ratio 1 : 1·18 : 1·33 and the molal volumes in a ratio 1 : 0·83 : 0·68, the values $\sigma^{1/4}$ change only in a ratio 1 : 1·08 : 1·13 which is less than one half of the change observed for the densities. When the molal volumes are compared with the evaluated parachor values, the change observed for the parachors amounts only to one third. According to this result, the parachor as a structurally determined quantity should be placed somewhere between the molal volume of the substance (sensitively reflecting the structural effects within the limits given by the temperature dependence) and its molecular mass which is within the attainable experimental accuracy insensitive to the structural changes at all.

This conclusion was tested in more detail by Exner who evaluated in a refined approach, from the experimental data on individual liquid compounds, the additive atomic, group and bond increments in their molal volumes[2] and parachors[10] (the latter taken for $y = 4$). The ratios of both these quantities are presented in Table III.

One can see that while for the atomic and functional groups the ratio of the parachor and the volume increments varies between 2 to 3 (for di-covalent groups bonded to two carbon atoms, as *e.g.* CO, S, NH, this ratio is as high as 4 which means that these groups increase the surface tension in increased extent), for the bond increments this ratio does not exceed number 1. This supports the theoretical conclusion that the participation of the surface tension in the formula of the parachor compensates (for suitably chosen exponent $1/y$) not only the temperature dependence of the molal volume of a substance but partly also the structural effects. However, with the exponent 1/4, the surface tension does not prevail over the structural effects in the molal volume of the substance and it is only weakening them.

As far as the additivity of the contributions of the structural elements to the parachor of a substance is concerned, the analysis of the experimental data[10] supports, too, the conclusions of the former theoretical considerations. The experimentally determined increments for the parachors of one and the same group (CH_2) remain constant in the same homological series (within the limits of experimental error) even after elimination of the effects introduced into the results by the additivity of the atomic masses M. However, in the homological series of different types, these increments can be markedly different one from another (unlike the increment in the molal volume or specific volume $1/\varrho_1$ itself). From the cited analysis[10], one can see that in the case of the halogenated derivatives they are higher than in the case of the pure hydrocarbons while with oxygen derivatives it is the other way around.

Additivity of the Parachors of Substances in Mixtures

From the way in which equation (*22*) was obtained, it is clear that the additivity of the parachors of components cannot hold exactly (in contradiction to the molal volume) even in the case of ideal solutions. In order to obtain the additive relation (*22*) for ideal mixtures, it was necessary to introduce even for these mixtures a number of approximations. This does not mean that the additivity rules – in whichever way they are not exact – cannot be of diagnostic use in the cases where the substance itself cannot exist as a liquid with the same structure with which it exists in solutions where the surface tension is easily measurable while other physical parameters (like refraction, electric conductivity, permittivity, infrared adsorption *etc.*) can be measured only with difficulty or without a required resolving power. This is exactly the case of strong electrolytes and their complex species in aqueous solutions, especially then in the region of very high concentrations.

As shown above, in such a case, we obtain instead of the parachor of the studied form itself only the corresponding "apparent" parachor Π_1, including the changes of the parachor of the solvent caused by solvent–solute interactions. Qualitatively one may expect that the physical cohesive interaction between these two components

TABLE III

The relation of additive atomic, group and bond increments Δ, of the parachor[10] to molar volume increments[2], expressed by ratio $\Delta P/\Delta V$

Structural element	$\Delta P/\Delta V$	Structural element	$\Delta P/\Delta V$	Structural element	$\Delta P/\Delta V$
CH_2	2·4	OH (prim.)	2·9	cyclo-(C_6H_{11})	2·4
CH_3	1·8	SH (prim.)	2·6	$CH_2{=}CH$	2·0
F (prim.)	1·8	NH_2 (prim.)	2·5	$CH{\equiv}C$	2·2
Cl (prim.)	2·4	CHO	2·5	C_6H_5	2·5
Br (prim.)	2·7	COOH	2·7	$C_{10}H_7$, pyridyl	2·7
I (prim.)	2·8	CO (ket.)	4·3	double bond	0·9
CN (prim.)	2·8	S (sulphid.)	4·4	triple bond	1·0
NO_2	3·0	NH (sec)	3·8	6-ring (alic.)	0·3

which results in contraction of the apparent volume of the solute, will lead simultaneously to increased surface tension of the solution as a whole, as a consequence of increased separation work $\bar{w}_\sigma$. This can be useful for elimination of the physical effects caused in the apparent volume of the dissolved substance, by its interaction with the solvent. The parachor might be, for this reason, regarded as an advantageous tool for investigation of the chemical structure of the electrolytes (and of their chemical transformations) in concentrated aqueous solutions in which the above interaction is extraordinary strong. The limits for such applications can be naturally specified only experimentally.

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