## NEW POSSIBILITIES OF APPLICATIONS OF THE BARKER QUASI-LATTICE THEORY. SOME RELATIONS BETWEEN EXCESS FUNCTIONS AT INFINITE DILITION

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A relation for the limiting activity coefficient and for the partial excess enthalpy of binary solution was derived from the Barker quasi-lattice theory. On the basis of these equations we found the relations between  $\gamma_i^\infty$  or  $h_i^{E\infty}$  for some groups of related binary systems in an especially simple form so that is it possible to convert these quantities from one system to another without the evaluation or knowledge of adjustable energy parameters. For some predictions it is only necessary to choose a geometrical model of molecules involved in them. The relations were obtained for binary systems whose one component is formed by monotonous molecules varying in size (such as n-alkanes) and the other component is arbitrary. A very simple relation also holds for limiting activity coefficients of substances forming homologous series in two arbitrary solvents. The practical utility and accuracy of the relations obtained is demonstrated on a number of examples. The agreement with experimental data is excellent for absolute majority of the systems tested.

The values of excess thermodynamic functions at infinite dilution represent to a considerable extent limited but still very valuable information on the behaviour of binary systems of non-electrolytes. In many cases they can be obtained relatively easily by a rapid experimental technique. From the practical point of view these quantities represent condensed data on the extent of non-ideality of a system which are suitable for constructing the correlations of system properties with the structure of components involved. For limiting activity coefficients, in this respect, e.g. the Pierroti, Deal and Derr correlation<sup>1</sup>, the correlation based on the solubility parameter concept<sup>2-4</sup> or on the group contribution concept<sup>5</sup> as the ASOG (ref.<sup>6</sup>) and UNIFAC (ref.<sup>7</sup>) methods are known. The limiting values of thermodynamic functions are also suitable testing properties for proposed theoretical models of solutions. In this work we deal with some relations between limiting activity coefficients or relations between limiting partial excess enthalpies, respectively, resulting from the Barker quasi-lattice theory, we test them and discuss their practical applicability.

## THEORETICAL

If we use in the Barker quasi-lattice theory for the description of combinatorial effects the Guggenheim relation for athermal combinatorial factor  $g^*$ , the relation for the activity coefficient  $\gamma_A$  of a component A in a binary system with mole fraction  $x_A$  can be written down in the form<sup>36</sup>

$$\ln \gamma_{\rm A} = \sum_{i \in {\rm A}} Q_i \ln \left( X_i / x_{\rm A} X_i^{\rm A\, I} \right) + r_{\rm A} (z/2 - 1) \ln \left[ x_{\rm A} + \left( r_{\rm B} / r_{\rm A} \right) x_{\rm B} \right], \tag{1}$$

where  $r_A$ ,  $r_B$  are the numbers of segments of molecules A, B, each of them occupying one site on a lattice with coordination number z. The number of surface contact points of the type i is denoted by  $Q_i$  and the quantities  $X_i$  and  $X_i^{A1}$ , characterizing the numbers of binary contacts of the surface point of the type i, are simultaneous solution of the system of quasi-chemical equations and balance relations (see Eq. (9) in reference<sup>8</sup>). The expression for activity coefficient at infinite dilution is obtained by limiting Eq. (1) for  $x_A \to 0$ . If we realize that

$$\lim_{x_{A}\to 0} \frac{X_{i}}{x_{A}} = \lim_{x_{A}\to 0} \frac{Q_{i}/2}{\sum_{j} \eta_{ij} X_{j}} = \frac{Q_{i}/2}{\sum_{i \in B} \eta_{ij} X_{j}^{B1}} \quad (i \in A),$$
 (2)

for the limiting activity coefficient follows

$$\ln \gamma_{\rm A}^{\infty} = \sum_{i \in A} Q_i \ln \frac{Q_i/2}{X_i^{A1} \sum_{i \in B} \eta_{ij} X_j^{B1}} + r_{\rm A}(z/2 - 1) \ln (r_{\rm B}/r_{\rm A}), \qquad (3)$$

where  $\eta_{ij}$  are the Boltzmann factors corresponding to the interaction between the *i*-th and *j*-th surface point. The expression for  $\ln \gamma_B^{\infty}$  is obtained by replacing subscripts A by B in Eq. (3).

From the relation for heat of mixing (Eq. (3) in ref.<sup>8</sup>) it is possible to derive the relation for partial excess enthalpy at infinite dilution:

$$\begin{split} R_{\mathbf{A}}^{\mathrm{E},\mathrm{o}} &= \lim_{\mathbf{x}_{\mathbf{A}} \to 0} \frac{\partial h^{\mathrm{E}}}{\partial x_{\mathbf{A}}} = 2 \left[ -\sum_{\substack{i \in \mathbf{A} \\ i > j}} \sum_{\substack{j \in \mathbf{A}}} X_{i}^{\mathrm{A}1} X_{j}^{\mathrm{A}1} \eta_{ij} h_{ij} + \right. \\ &+ \sum_{\substack{l \in \mathbf{B} \\ l > m}} \sum_{\mathbf{m} \in \mathbf{B}} \left( X_{l}^{\mathrm{B}1} X_{m}^{\mathrm{B}1} + \left( \frac{\partial X_{1}}{\partial x_{\mathbf{A}}} \right) X_{m}^{\mathrm{B}1} + \left( \frac{\partial X_{m}}{\partial x_{\mathbf{A}}} \right) X_{1}^{\mathrm{B}1} \right) \eta_{1m} h_{1m} + \\ &+ \sum_{\substack{i \in \mathbf{A} \\ l \in \mathbf{B}}} \sum_{\mathbf{l} \in \mathbf{B}} \left( \frac{\partial X_{i}}{\partial x_{\mathbf{A}}} \right)^{\infty} X_{1}^{\mathrm{B}1} \eta_{11} h_{11} \right], \end{split}$$
(4)

where the symbol  $(\partial X_i/\partial x_A)^{\infty}$  denotes  $\lim \partial X_i/\partial x_A$  at  $x_A \to 0$ . By replacing subscripts A by B we obtain the relation for  $\overline{h}_n^{E\infty}$ .

Let us observe concerete cases now. I) Let the solute be an arbitrary component A, the solvent B is formed by n-alkanes of different length. Assuming that the molecules of n-alkanes have monotonous surface, uniform from the point of view of interactions with its environment and non-changing its properties by elongating the chain  $(\eta_{ij})$  does not change when exchanging n-alkane), it is possible to write  $\ln \gamma_A^{\infty}$  in the form

$$\ln \gamma_{A}^{\infty} = k_{A} - (\sum_{i \in A} Q_{i}/2) \ln Q_{B} + r_{A}(z/2 - 1) \ln r_{B},$$
 (5)

where  $k_A$  is dependent only on the solute and not on the length of n-alkane.

For  $h_A^{E,\infty}$  we obtain in this case from Eq. (4) (the second term corresponding to the interactions between different surface areas of the molecule B disappears with respect to its monotonicity)

$$h_{A}^{E\infty} = \sum_{\substack{i \in A \\ i \in A}} Q_{i}h_{ij} - 2 \sum_{\substack{i \in A \\ i > k}} \sum_{k \in A} X_{i}^{A1}X_{k}^{A1}\eta_{ik}h_{ik}.$$
 (6)

As the relation  $(\delta)$  does not comprise neither directly nor indirectly a characteristics of the dimension of the molecule of solvent B the limiting partial excess enthalpy should have the identical value for the given arbitrary solute in all n-alkanes.

2) Let the solute B be n-alkanes of different length, the solute A being arbitrary. On the assumption of monotonicity of the alkane molecules (likewise at the point 1) we can write for limiting activity coefficient of n-alkanes in accordance with Eq. (3)

$$\ln \gamma_{\rm B}^{\infty} = k_{\rm B} Q_{\rm B} + (Q_{\rm B}/2) \ln (Q_{\rm B}/2) + r_{\rm B}(z/2 - 1) \ln (r_{\rm A}/r_{\rm B}). \tag{7}$$

This relation makes it possible to calculate  $\gamma^{\infty}$  for any other n-alkane in some solvent from the knowledge of  $\gamma^{\infty}$  of one n-alkane in the same solvent.

Further it is possible to show easily that for all  $i \in A$ , B,  $(\partial X_1/\partial x_B)$  are linearly dependent on the number of surface contact points of n-alkane  $Q_B$ . Hence it follows, too, the linear dependence on  $Q_B$  for limiting partial excess enthalpy of n-alkane

$$h_{\rm B}^{\rm E\infty} = \alpha Q_{\rm B} \,, \tag{8}$$

where  $\alpha$  is independent of the n-alkane length.

3) Let us assume limiting activity coefficients of members of some homologous series (e.g. n-alcohols, 1-alkenes, and the like),  $\gamma_{A(C)}^{\infty}$ ,  $\gamma_{A(C)}^{\infty}$  in binary solutions of two arbitrary solvents B and C. If we denote the number of surface contact points of the n-alkyl type in solute by  $Q_1$ , the relation holds according to Eq. (3) for the values of these limiting activity coefficients

$$\ln \frac{\gamma_{A(C)}^{\infty}}{\gamma_{A(C)}^{\infty}} = Q_{1} \left[ \left( \sum_{j \in C} \eta_{1j} X_{j}^{C1} \right) / \left( \sum_{k \in B} \eta_{1k} X_{k}^{B1} \right) + \frac{1}{2} \ln \left( r_{B} / r_{C} \right) \right] + \\
+ \left\{ \sum_{\substack{i = 1 \ i \in A}} Q_{i} \ln \left[ \left( \sum_{j \in C} \eta_{ij} X_{j}^{C1} \right) / \left( \sum_{k \in B} \eta_{ij} X_{k}^{B1} \right) \right] + \\
+ \left( \sum_{\substack{i = 1 \ i \in A}} Q_{i} / 2 - 1 \right) \ln \left( r_{B} / r_{C} \right) \right\} = \alpha' Q_{1} + \beta' , \tag{9}$$

where  $\alpha'$ ,  $\beta'$  are independent of  $Q_1$ .

In accordance with the conclusions of our foregoing paper it is possible to reach results analogous to those given at the points 1,2 and 3 also on the basis of the generally formulated concept of group contributions.

## RESULTS AND DISCUSSION

The relations derived have been tested by using experimental data available in the literature. The used experimental data on limiting activity coefficients were altogether measured by the gas chromatography methods; the limiting partial excess enthalpies were measured calorimetrically or derived from chromatographic measurements. For the case when the solvents are n-alkanes we have used the geometric model accepted in our previous work8. In the case when n-alkanes form solutes at infinite dilution we have found, on the basis of preliminary calculations, as a rule, a qualitative agreement with the trend of experimental data. The quantitative agreement has been, however, relatively worse - the deviations have often amounted to 25 per cent of  $\gamma^{\infty}$  or even more. The improvement has not been possible to reach generally by changing the coordination number nor by changing the chosen size of solvent molecule. The quantitative agreement with experimental data can be, however, easily attained by changing  $r_m$ , i.e. by a change of the number of segments which are taken by medium group of molecule. We have chosen  $r_{\rm m}$  according to the character of system from 1 to 1/5. For the systems where the solvent molecule is relatively considerably smaller than the n-alkane dissolved,  $r_m \approx 1 - 1/2$ ; if the dimension of the solvent molecule and the dissolved n-alkanes is roughly the same  $r_m \approx 1/3$  and in the case that the solvent has considerably larger molecules it is possible to choose  $r_{\rm m} \approx 1/4 - 1/5$ . This empirical choice of  $r_{\rm m}$  is physically unreal and introduces a certain inconsistency into the model used. On the other hand, however, it enables, on retaining the original formalism (7), a comparatively accurate extrapolation and interpolation of limiting activity coefficients of n-alkanes in different solvents. The most probable reason why it is not possible to attain so good results at consistent choice of the geometric properties of molecules involved, is a wrong description of the combinatorial contribution to the activity coefficient. In this respect it might be possible to try other relations for  $g^*$  presented in the literature<sup>32,33</sup>. However, the

Table I Comparison of Relation (5) with Experimental Values of ln  $\gamma_A^{\infty}$ 

Solute		Calvant	Dof	100		2 4	$\tilde{\delta}^b$
r <sub>A</sub>	, °C	Solvent	Ref.	ln γ <sub>A</sub> ∞	k <sub>A</sub>	$\delta_{\max}^{a}$	δ <sup>-</sup>
1-Chlorobutan 3·5	e 76	n-C <sub>24</sub> n-C <sub>30</sub> n-C <sub>36</sub>	9 9 9	0·134 0·274 0·414	13·824 13·835 13·829	0.011	0.007
1-Chloropentar 4	ne 76	n-C <sub>24</sub> n-C <sub>30</sub> n-C <sub>36</sub>	9 9 9	-0.101 $-0.248$ $-0.355$	15·280 15·278 15·300	0.022	0.015
1-Chlorohexan 4·5	e 76	n-C <sub>24</sub> n-C <sub>30</sub> n-C <sub>36</sub>	9 9 9	0.071 0.224 0.322	16·734 16·719 16·746	0.027	0.018
1-Chlorohepta 5	ne 76	n-C <sub>24</sub> n-C <sub>30</sub> n-C <sub>36</sub>	9 9 9	-0.051 -0.189 -0.301	18·178 18·172 18·178	0.006	0.004
1,1-Dichloroet	hane 76	n-C <sub>24</sub> n-C <sub>30</sub> n-C <sub>36</sub>	9 9 9	0.051 0.203 0.354	13·906 13·906 13·889	0.017	0.011
1,2-Dichloroet	hane 76	n-C <sub>24</sub> n-C <sub>30</sub> n-C <sub>36</sub>	9 9 9	0·193 0·040 −0·113	12·726 12·732 12·711	0.021	0.014
1-Bromopropa 3	ne 76	n-C <sub>24</sub> n-C <sub>30</sub> n-C <sub>36</sub>	9 9 9	-0·185 -0·341 -0·489	12·348 12·351 12·341	0.010	0.007
1,3-Dibromopi 3·5	ropane 76	n-C <sub>24</sub> n-C <sub>30</sub> n-C <sub>36</sub>	9 9 9	0·794 0·617 0·458	14·751 14·726 14·701	0.050	0.033
Ethanol 2·5	50	n-C <sub>7</sub> n-C <sub>10</sub> n-C <sub>18</sub> n-C <sub>24</sub>	11 11 10 10	3·16 3·01 2·68 2·52	13·614 13·600 13·593 13·629	0.036	0.020
n-Propanol	50	n-C <sub>18</sub> n-C <sub>24</sub>	10 10	2·53 2·36	14·878 14·893	0.015	0.015
Methyl acetate	50	n-C <sub>18</sub> n-C <sub>24</sub>	10 10	0·99 0·78	14·773 14·737	0.036	0.036
Methyl format	e 50	n-C <sub>18</sub> n-C <sub>24</sub>	10 10	1·18 0·97	13·528 13·503	0.025	0.025
Acetone 3	50	n-C <sub>18</sub> n-C <sub>24</sub>	10 10	1·46 1·25	13·808 13·783	0.025	0.025

TABLE {
(Continued)

t, °C 50 100	n-C <sub>18</sub> n-C <sub>24</sub> n-C <sub>22</sub> n-C <sub>24</sub>	10 10 12	ln γ <sub>A</sub> <sup>∞</sup> 0.98 0.80	13·328	δ <sub>max</sub> <sup>a</sup>	$\bar{\delta}^b$
	n-C <sub>24</sub> n-C <sub>22</sub>	10		13.328	0.005	0.005
	n-C <sub>24</sub> n-C <sub>22</sub>		0.80			0.005
100		12	0.00	13.333		
100	n-C24	12	-0.152	15.177		
		12	-0.222	15.159		
	n-C <sub>28</sub>	12	-0.307	15.173		
	n-C <sub>30</sub>	12	-0.340	15.187	0.048	0.022
	n-C <sub>32</sub>	12	-0.373	15.198		
	n-C <sub>34</sub>	12	-0.408	15.206		
	n-C <sub>36</sub>	12	0.448	15.207		
	n-C <sub>22</sub>	12	-0.113	16.643		
100	n-C <sub>24</sub>	12	0.185	16.620		
	n-C <sub>28</sub>	12	-0.264	16.635		
		12	0.297	16.646	0.050	0.02
	n-C <sub>32</sub>	12	-0.327	16.659		
	n-C <sub>34</sub>	12	-0.362	16.655		
	n-C <sub>36</sub>	12	-0.397	16-670		
	n-C <sub>22</sub>	12	-0.076	18-107		
100		12	-0.158	18.072		
		12	-0.228	18.090		
		12	-0.259	18.102	0.052	0.02
		12	-0.284	18.118		
		12	-0.317	18-124	. ~ ~	
	n-C <sub>36</sub>	12	-0.355	18-124		
	n-C24	13	-0.128	20.949		
80	n-C <sub>30</sub>	13	-0.222	20.973	0.032	0.01
	n-C <sub>32</sub>	13	-0.247	20.985		
		13	-0.323	20.981		,
		n-C <sub>34</sub> n-C <sub>36</sub> n-C <sub>22</sub> n-C <sub>24</sub> n-C <sub>30</sub> n-C <sub>32</sub> n-C <sub>34</sub> n-C <sub>34</sub> n-C <sub>36</sub> n-C <sub>24</sub>	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

<sup>&</sup>lt;sup>a</sup> Maximum absolute deviation in  $\ln \gamma_A^{\infty}$ , <sup>b</sup> average absolute deviation in  $\ln \gamma_A^{\infty}$ .

mentioned error of the combinatorial contribution need not be too weighty at finite concentrations. (Let us mention in addition to it that in our foregoing paper, in which we dealt with the prediction of  $G^E$ , the choice  $r_m = 1/2$  should comply relatively well according to the above-mentioned rules for all the systems investigated.)

The results of testing the relations (5) and (7) are given in Tables I and II partly in the form of constants  $k_A$  and  $k_B$  calculated from single limiting activity coefficients,

Table II  $\label{eq:comparison} \mbox{Comparison of Relation (7) with Experimental Values of ln $\gamma_B^\infty$ }$ 

Solvent		Solute	Ref.	ln γ <sup>∞</sup>	$-k_{\rm B}$	$\delta_{\rm max}$
r <sub>A</sub> <sup>a</sup>	t, °C	Solute		тт /в	^в	max
Phenol		n-C <sub>5</sub>	14	2.54	0.7405	
11/4	25	n-C <sub>6</sub>	14	2.72	0.7414	0.03
•		n-C <sub>7</sub>	14	2.93	0.7397	
Benzonitrile		n-C <sub>5</sub>	14	1.69	0.8427	
12/4	25	n-C <sub>6</sub>	14	1.82	0.8430	0.0
		n-C <sub>7</sub>	14	1.93	0.8441	
Diethylene g		n-C <sub>5</sub>	15	4.16	0.7618	
11/3	50	n-C <sub>6</sub>	15	4.52	0.7651	
		n-C <sub>7</sub>	15	4.92	0.7649	0.0
		n-C <sub>8</sub>	15	5.34	0.7633	
		n-C <sub>9</sub>	15	5.71	0.7641	
		n-C <sub>10</sub>	15	6.10	0.7636	
2-Pentanone		n-C <sub>5</sub>	16	1.66	1.0459	
. 9/2	20	n-C <sub>6</sub>	16	1.88	1.0465	0.0
		n-C <sub>7</sub>	16	2.14	1.0443	
n-Butanol		n-C <sub>5</sub>	14	1.40	0.8729	0.0
9/3	25	n-C <sub>7</sub>	14	1.64	0.8736	
Dimethyl su	Iphoxide	n-C <sub>5</sub>	14	4.12	0.6285	
8/3	25	n-C <sub>6</sub>	14	4.43	0.6324	0.0
		n-C <sub>7</sub>	14	4.80	0.6322	
Squalane		n-C <sub>4</sub>	17	<b>-</b> 0⋅548	1.4032	
38/5	20	n-C <sub>5</sub>	17	-0.483	1.4010	0.0
		n-C <sub>6</sub>	17	<b></b> 0·454	1.4016	
		n-C <sub>7</sub>	17	-0.399	1.3998	
Acetonitrile		n-C <sub>5</sub>	5	2.74	0.8422	
3/1	24	n-C <sub>6</sub>	5	2.97	0.8483	
		n-C <sub>16</sub>	5	5.92	0.8469	0.1
		n-C <sub>22</sub>	5	7.44	0.8466	
		n-C <sub>32</sub>	5	10.87	0.8382	
Diethyl phthalate		n-C <sub>5</sub>	15	1.37	1.1238	
22/4	50	n-C <sub>6</sub>	15	1.50	1.1256	
		n-C <sub>7</sub>	15	1.65	1.1254	0.0
		n-C <sub>8</sub>	15	1.79	1.1256	
		n-C <sub>9</sub>	15	1.92	1.1260	
		n-C <sub>10</sub>	15	2.07	1.1252	
Triethylene	glycol	n-C <sub>6</sub>	19	4.47	0.7770	
16/4	29,5	n-C <sub>7</sub>	19	4.78	0.7788	0.0
		n-C <sub>8</sub>	19	5-14	0.7769	

TABLE II
(Continued)

Solvent		Color	D 6		4.	2
r <sub>A</sub> ª	t, °C	- Solute	Ref.	ln γ <sub>B</sub> <sup>∞</sup>	- k <sub>B</sub>	$\delta_{\max}^{b}$
n-C <sub>24</sub>		n-C <sub>5</sub>	13	0.273	1-3120	
32/5	60	n-C <sub>6</sub>	13	-0.242	1.3126	
		n-C <sub>7</sub>	13	-0-201	1.3120	0.01
		n-C <sub>8</sub>	13	-0·177	1.3124	
		n-C <sub>10</sub>	13	-0.128	1.3125	
n-C <sub>20</sub>		n-C <sub>5</sub>	13	0.188	1.2492	
28/5	40	n-C <sub>6</sub>	13	-0.161	1.2498	0.01
		n-C <sub>7</sub>	13	-0.134	1.2500	
n-C36		n-C <sub>5</sub>	13	-0.501	1.4640	
44/5	80	n-C <sub>6</sub>	13	-0.459	1.4641	
		n-C <sub>7</sub>	13	-0.423	1.4644	0.01
		n-C <sub>8</sub>	13	-0.383	1.4641	
		n-C <sub>10</sub>	13	-0.323	1.4642	
Methanol		n-C <sub>3</sub>	20	2.456	0.5871	0.02
6/3	25	n-C <sub>4</sub>	20	2.695	0.5890	
Ethanol		n-C <sub>3</sub>	20	1.850	0.7041	0.06
7/3	25	n-C <sub>4</sub>	20	2.003	0.7086	
Isopropanol		n-C <sub>3</sub>	20	1.484	0.7966	0.04
11/4	25	n-C <sub>4</sub>	20	1.592	0.8029	

<sup>&</sup>lt;sup>a</sup> Denominator of the fraction corresponds to the choice of  $r_m$ , <sup>b</sup> maximum absolute deviation in  $\ln \gamma_B^{\infty}$ .

partly as the maximum or average deviations of the prediction of one data  $\ln \gamma^{\infty}$  from the other. In most cases the average deviation of the prediction does not exceed 2 per cent of  $\gamma^{\infty}$ . In connection with gas chromatography, the use of relation (5) appears as especially promising for practical prediction of vapour-liquid equilibrium. From the value of  $\gamma^{\infty}$  of arbitrary volatile substance in a non-volatile longer n-alkane, which is easily available by the current technique of gas chromatography (n-alkane forms the stationary phase), it is possible to calculate according to Eq. (5) the limiting activity coefficient of the same substance in a volatile shorter n-alkane which is for a change mostly more interesting from the practical point of view. In connection with some of one-parameter equations for  $G^{\rm E}$  (ref.  $^{34}$ ,  $^{35}$ ) this procedure would represent a simple, rapid, effective method for predicting VLE of binary systems with n-alkanes which needs a minimum of experimental data.

To carry out the test of relations (6), (8) and (9) it is not necessary to specify the geometric model of the lattice and molecules involved. The independence of the limiting partial excess enthalpy of solute of the special type  $B_mC_n$  of the length of n-alkane  $B_1$  as a solvent had been already derived by Sheller and coworkers that starting from the group contribution concept. For several solutes they had presented chromatographically determined  $h_A^{E\infty}$  in two n-alkane solvents  $C_{18}H_{38}$  and  $C_{24}H_{50}$  which are within the range of experimental errors the same. Savini and coworkers had found from calorimetric determination of heats of mixing the constant value of  $h_A^{E\infty}$  for n-octanol in n-alkanes equal 21.8 kJ/mol and for ethanol in n-alkanes of diluted solutions of n-propanol and n-hexanol in n-alkanes, the values of  $h_A^{E\infty}$  of diluted solutions of n-propanol and n-hexanol in n-alkanes, the values of  $h_A^{E\infty}$  24.2 kJ/mol and 23.4 kJ/mol, resp., Woycicka and Kalinovska and found out even a constant value of  $h_A^{E\infty}$  for n-decanol in n-alkanes. Further proofs can be provided e.g. for benzene  $h_A^{E\infty}$  esters the experimental data in the literature.

TABLE III

Illustration of Linear Dependence of  $\ln (\gamma_{A(B)}^{\infty})/\gamma_{A(C)}^{\infty}$  on the n-Alkyl Chain Length of Molecule A

Set <sup>a</sup>	Solute	$\ln  (\gamma^{\infty}_{\mathbf{A}(B)}/\gamma^{\infty}_{\mathbf{A}(C)})$	$\Delta_1^{\ b}$	
	n-butane	3.26	0.19	
1	n-pentane	3.47	0.20	
	n-hexane	3.67	0.21	
	n-heptane	3.86		
	n-pentane	1.52	0.24	
2	n-hexane	1.76	0.22	
_	n-heptane	1.98	0.22	
	n-octane	2.20		
	1-pentene	2.40	0.28	
3	1-hexene	2.68	0.28	
_	1-heptene	2.96	0.29	
	1-octene	3.25		
	n-pentane	2.74	0.19	
	n-hexane	2.93	0.23	
4	n-heptane	3.16	0.25	
	n-octane	3.41	0.24	
	n-nonane	3.65	0.25	
	n-decane	3.90		

<sup>&</sup>lt;sup>a</sup> Set 1: B = aniline, C = squalane,  $20^{\circ}$ C, ref.<sup>30</sup>, set 2: B = aniline, C = 1-methylnaphthalene,  $20^{\circ}$ C, ref.<sup>30</sup>, set 3: B = diethylene glycol, C = diethyl phthalate,  $75^{\circ}$ C, ref.<sup>31</sup>, set 4: B = diethylene glycol, C = diethyl phthalate,  $75^{\circ}$ C, ref.<sup>31</sup>; <sup>b</sup> first (relative) differences.

The linear dependence of  $h_{\rm B}^{\rm E,\infty}$  on the number of surface contact points of n-alkanes, i.e. in fact on the number of carbon atoms of the alkane chain  $n_{\rm c}$  is demonstrated in Fig. 1 on experimental data of various systems.

As a test of relation (9) we present Fig. 2 and Table III. With respect to the deficiency of data of needed type we have been forced to choose as a general homologous series mostly n-alkanes or 1-alkenes and only exceptionally n-alcohols or 1-chloro-alkanes. In all the cases investigated, the dependence of  $\ln \left( \gamma_{a(B)}^{\infty} / \gamma_{A(C)}^{\infty} \right)$  on the number of carbons of the n-alkane chain is linear with considerable accuracy.

F1G, 1

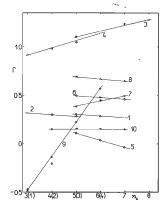
Dependence of Partial Excess Enthalpy at Infinite Dilution  $\overline{h}_{B}^{E\infty}$  (kJ/mol) of n-Alkanes in Different Solvents on the Number of Carbon Atoms of n-Alkanes  $r_{e}$ 

1 Acetone, -20°C, ref.<sup>26</sup>, 2 methanol, 25°C, ref.<sup>26</sup>, 3 2-ethylhexyl phthalate, 50°C, ref.<sup>27</sup>, 4 butyl benzyl phthalate, 50°C, ref.<sup>27</sup>, 5 dimethyl sulphoxide, 25°C, ref.<sup>26</sup>.

Fig. 2

Dependence of  $\Gamma = \ln \left( \gamma_{A'B)}^{\infty} / \gamma_{A(C)}^{\infty} \right)$  on the Number of Carbon Atoms  $n'_c$  of n-Alkyl Chain

1 An-alkanes, Beicosane, Csqualane, 53.2°C, ref. 18, 2 A 1-alkenes, B eicosane, C squalane, 53.2°C, ref. 18, 3 A n-alkanes, B diethyl phthalate, C dibutyl phthalate, 25°C, ref. 28, 4 A 1-alkenes, B diethyl phthalate, C dibutyl phthalate, 25°C, ref. 28, 5 A n-alkanes, B sulpholane, C dimethyl sulphoxide, 30°C, ref. 19, 6 A n-alkanes, B sulpholane, C propylene carbonate, 30°C, ref. 19, 7 A n-alkanes, B dimethyl sulphoxide, C propylene carbonate, 30°C, ref. 19, 8 A n-alkanes, B triethylene glycol, C propylene carbonate, 30°C, ref. 19, 9 A n-alcohols, B glycerol, C oxydipropionitrile, 60°C, ref. 29 (ne values in parentheses), 10 A 1-chloroalkanes, B n-C<sub>24</sub>, C n-C<sub>30</sub>, 80°C, ref. 9.



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