

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Density, Concentration and Orientation Inhomogeneities of the Surface Layer of n-Alkanes.

Victor A Dozorov*.

Nosov Magnitogorsk Technical State University, 455000, 38 Lenin ave., Magnitogorsk, Russia.

ABSTRACT

A previously developed multilayer lattice model of the surface layer for r-dimensional systems with vacancies for n-alkanes has been applied. Using the obtained correlations, we have calculated the density profile, concentration and orientation inhomogeneities of the surface layer of pure n-alkanes and their mixtures. We have also explained the dependency of the surface properties of such systems on their composition and temperature. In this work you can familiarize yourself with professor and corresponding member of the Russian Academy of Science Smirnova's theoretical conception as well as with the results of the author's independent scientific research into the development of the concept itself.

Keywords: n-alkanes and their mixtures, multilayer lattice model, vacancies, n-paraffins, r-mers, electronic diffraction, orientation inhomogeneity of the surface area.

**Corresponding author*

INTRODUCTION

In the series of professor Smirnova and her other co-authors' work [1-4], there have been considered issues related to the calculation of the concentration and orientation inhomogeneities of the surface layer of r -dimensional mixtures and associated solutions of r -mers based on the latticed model within Barker approximation [5].

As a contribution to the research into r -mer systems in general and n -alkane mixtures in particular, there has been carried out a series of work [6-10] which allows within a multilayer lattice model of the surface of the area with vacancies to calculate the density profile, concentration and orientation inhomogeneities of the surface layer of pure n -alkanes and their mixtures, as well as to explain the dependency of the surface properties of such systems on their composition and temperature.

MATERIALS AND METHODS

The calculation method complied with the one described in work [11], and at the same time considering presence of vacancies (holes) in the system has become a new element. Consequently, we have had to reconsider the number of positions occupied by the holes in the bulk phase of pure r -mers and their mixtures which was done using the experimental results that were obtained in the research of the structure of n -paraffins using the methods of electronic diffraction [12] and ultra-sound [13].

We see an n -alkane molecule as a set of interconnected segments CH_3 - and CH_2 - which have non-specific (ordinary) and specific (taking part in the formation of a chemical bond between the segments) contact parts. The composition of monolayers parallel to the liquid-vapor interface is characterised by variables $\varphi_i^{(p)}$, where p is a layer number (the layers are numbered according to the distance from the interface), $i = \text{CH}_2$, CH_3 , B (a hole). The orientation inhomogeneity of the surface area is estimated through a relation of the molecular contact areas of a certain type which face the inside of a particular layer to the preceding or consequent layers (9).

According to the model, the calculations that were done for liquid n -alkanes C_6 - C_{18} within a temperature range of 20-170°C have proved about 20-30 monolayers close to the boundary with vapor to be different in terms of their components, density and orientation properties from the homogeneous volume phase, the more so significant difference is limited by 2-3 monolayers.

In the first layer of the surface phase the number of seats occupied by holes (volume concentration of holes) exceeds the similar index in the volume phase approximately 1,6-2,8 folds. The comparative number of CH_3 - groups for the first layer is almost 1,2-1,7 times as big comparing with the volume phase, so it can be considered that the surface layer at the vapor-liquid interface is rich in end groups of an r -mer. According to the calculation, the fragment "an end CH_3 - element in the first layer – a CH_2 - segment connected to it" is oriented mainly perpendicularly, whereas parallel orientation in the first layer can be met more rarely than that of in the further layers.

A decrease in the volume fraction of CH_2 particles in the first layer of the surface phase related to the same parameters mentioned equals to 60-70% conditional on the increased part of end groups CH_3 - in the first layer as well as the fact that the CH_3 - group occupies a bigger volume in comparison with the CH_2 - group or a hole (14).

Table 1: Density of surface phase layers of tetradecane at 20–800C, g/cm³.

Layer number, p	Temperature, °C						
	20	30	40	50	60	70	80
1	0,5673	0,5516	0,5372	0,5254	0,5136	0,5019	0,4898
2	0,7050	0,6912	0,6847	0,6784	0,6721	0,6660	0,6599
3	0,7158	0,7014	0,6949	0,6887	0,6824	0,6763	0,6701
4	0,7269	0,7120	0,7056	0,6992	0,6929	0,6866	0,6803

5	0,7369	0,7213	0,7147	0,7081	0,7016	0,6951	0,6886
6	0,7454	0,7293	0,7224	0,7156	0,7089	0,7022	0,6954
7	0,7523	0,7357	0,7287	0,7217	0,7148	0,7079	0,7009
8	0,7577	0,7409	0,7337	0,7266	0,7195	0,7125	0,7054
9	0,7618	0,7449	0,7377	0,7305	0,7233	0,7162	0,7089
10	0,7649	0,7480	0,7407	0,7335	0,7263	0,7191	0,7117
11	0,7672	0,7503	0,7431	0,7358	0,7285	0,7213	0,7138
12	0,7689	0,7520	0,7448	0,7376	0,7302	0,7230	0,7155
13	0,7701	0,7533	0,7461	0,7389	0,7316	0,7243	0,7167
14	0,7709	0,7542	0,7471	0,7399	0,7325	0,7252	0,7177
15	0,7715	0,7549	0,7478	0,7406	0,7333	0,7260	0,7184
16	0,7719	0,7553	0,7483	0,7411	0,7338	0,7265	0,7190
17	0,7721	0,7557	0,7486	0,7415	0,73422	0,7269	0,7194
18	0,7723	0,7559	0,7489	0,7417	0,7347	0,7272	0,7197
19	0,7724	0,7560	0,7491	0,7419	0,7348	0,7274	0,7199
20	0,7725	0,7561	0,7492	0,7421	0,7348	0,7276	0,7201
21	0,7726	0,7562	0,7493	0,7421	0,7349	0,7277	0,7202
22		0,7563	0,7493	0,7421	0,7350	0,7278	0,7203
23			0,7494	0,7422	0,7350	0,7278	0,7203
24				0,7422	0,7351	0,7279	0,7204
25					0,7351	0,7279	0,7204
26						0,7280	0,7204
27							0,7204
28							0,7204
Volume, ρ	0,7727	0,7564	0,7495	0,7423	0,7352	0,7280	0,7205

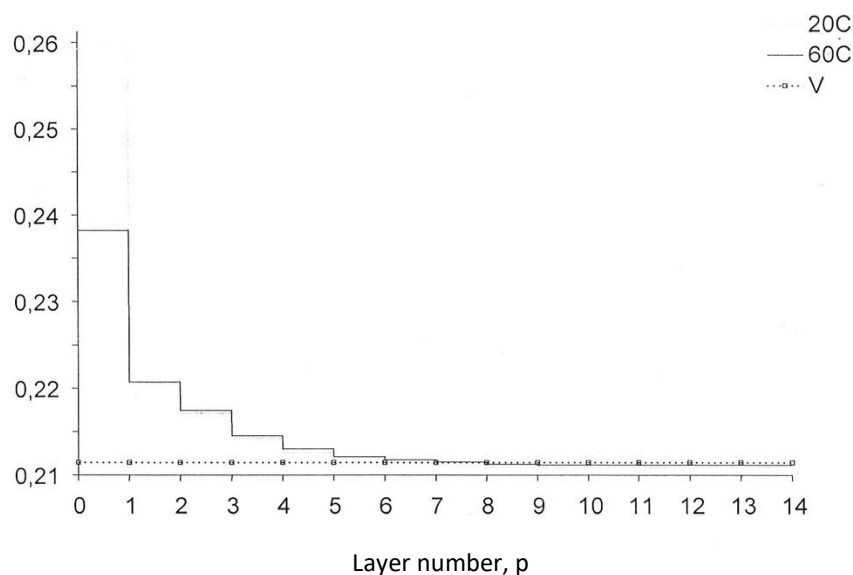
 Part of CH₃- groups; $\rho_{CH_3}^{(p)}$


Fig 1: Concentration profile of the surface layer of tetradecane (20 – 60°C) in relation with CH₃- groups; V – variable value in layer volume.

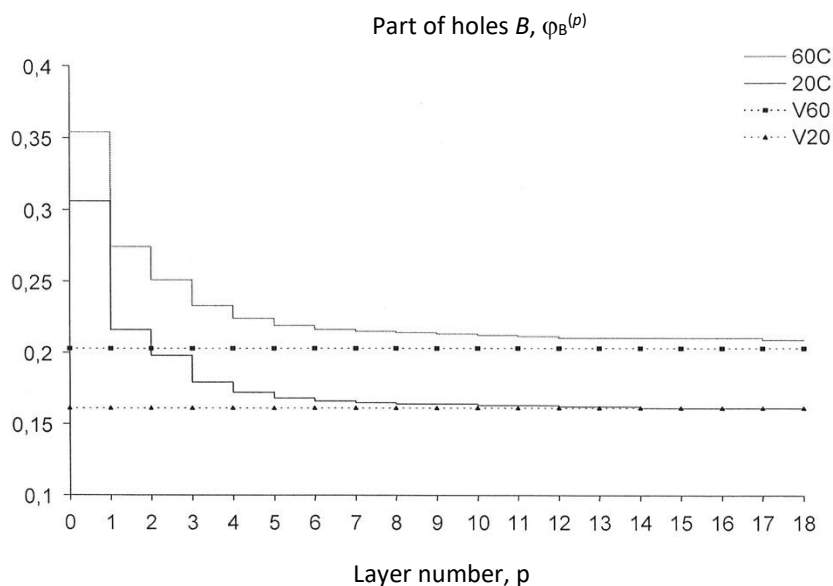


Fig 2: Concentration profile of the surface layer of tetradecane (20 – 60°C) in relation with holes; – variable value in layer volume.

An increase in the number of seats occupied by holes in layer p means a decrease in its density $\rho^{(p)}$. In Table 1 you can find density profiles for tetradecane at different temperatures. The concentration profile for CH_3 - groups and holes at the same temperatures is given in Figures 1 and 2. As it can be seen from Table 1, the density of the first five layers is 1,2-1,5 times as low as the density of the volume phase (ρ), this difference increasing with the temperature rise. The value of density $\rho^{(p)}$ monotonously approximates the volume value ρ , the layer number p increasing, so when it comes to the layer number $p = 16-20$, there is practically no difference (Table 1). It is only for the first 2-3 layers that error for values $\rho^{(p)}$ and volume value ρ can be considered significant.

In the first layer of the inhomogeneous area of a liquid n -alkane, the part of the seats occupied by the CH_3 -groups (Fig.1) and holes (Fig.2) exceeds the same parameter for the volume phase by approximately 20-100%, and with the increase in temperature the number of holes in numbered layers 1,2 significantly goes up, which corresponds with some general scientific conceptions.

For a specific temperature while moving away from the separating surface, the number of holes monotonously (for $p = 4-20$) reaches the number of holes in the volume phase.

Table 2: Density of layers of surface phase of n -alkanes at temperature 70°C, g/cm^3

Layer number, p	Number of carbon atoms in r -mer molecule chain of n -alkane				
	C_8	C_{10}	C_{13}	C_{14}	C_{18}
1	0,5227	0,5159	0,5061	0,5019	0,4736
2	0,5977	0,6318	0,6585	0,6660	0,6854
3	0,6143	0,6427	0,6690	0,6763	0,6959
4	0,6274	0,6526	0,6793	0,6866	0,7068
5	0,6371	0,6609	0,6878	0,6951	0,7152
6	0,6443	0,6678	0,6948	0,7022	0,7219
7	0,6495	0,6732	0,7006	0,7069	0,7274
8	0,6532	0,6775	0,7051	0,7125	0,7318
9	0,6557	0,6808	0,7087	0,7162	0,7353
10	0,6575	0,6833	0,7115	0,7191	0,7382
11	0,6586	0,6852	0,7137	0,7213	0,7404
12	0,6594	0,6866	0,7154	0,7230	0,7421
13	0,6599	0,6876	0,7166	0,7243	0,7435

14	0,6602	0,6883	0,7175	0,7252	0,7445
15	0,6604	0,6888	0,7182	0,7260	0,7453
16	0,6605	0,6892	0,7187	0,7265	0,7460
17	0,6606	0,6895	0,7191	0,7269	0,7464
18	0,6607	0,6898	0,7194	0,7272	0,7468
19	0,6607	0,6899	0,7196	0,7274	0,7471
20	0,6608	0,6900	0,7197	0,7276	0,7473
21		0,6901	0,7198	0,7277	0,7474
22		0,6901	0,7198	0,7278	0,7475
23		0,6902	0,7199	0,7278	0,7476
24			0,7199	0,7279	0,7477
25			0,7200	0,7279	0,7477
26				0,7280	0,7478
27					0,7478
28					0,7478
29					0,7478
30					0,7479
Volume, ρ	0,6608	0,6902	0,7200	0,7280	0,7479

Beginning with the 4-5th layers, change in the layer structure and CH₃- and CH₂- groups orientation in the layer is minimal in comparison with the volume phase, and it smoothly turns into certain values for the volume phase after 20-30 layers.

The number of seats in CH₃- groups decreases with the rise in temperature in the layers nearest to the interface while the number of seats in CH₂- groups and holes increases, which corresponds to general physical concepts, i.e. equalizing of particle concentration in the surface phase relating to that of in volume is the result of acceleration in heat motion of molecules, whereas a decrease in layer density is connected to an increase in the volume fraction of holes in the surface layer, the temperature of the system rising.

With the rise in temperature we see an increase in the length of the surface phase, and at the same time, a transition to the values of the variables in the volume phase from layer to layer of the inhomogeneous phase becomes smoother and smoother (see Table 1).

As it becomes obvious from the calculations (9), with the extension of the molecule chain (from C₆ to C₁₈) the number of CH₃- groups in the surface layer as well as that of the holes per particle goes down. With the increase in the molecule chain of n-alkane in the first layer of the surface phase of a liquid n-paraffin, we see a decrease in the number of CH₃- end particles.

The longer an r-mer chain becomes, the longer the surface layer (for a certain temperature) is. However, a transition to a volume phase (except the first layer) is slower but steadier (Table 2).

Having carried out the research, it becomes possible to draw the following conclusions about the properties of the surface layer of liquid n-alkanes and their mixtures at the liquid-vapor interface: in terms of their structure, density and orientation inhomogeneities, it is only the first 2-3 layers that are very different from the volume phase, i.e. a relatively small surface area consisting of 2-3 layers plays a fundamental role in the formation of surface properties.

For n-alkane mixtures, a change in the first layer composition of the surface area is not that big in comparison with the volume phase. Effects connected with the existence of the separating surface result mostly in increasing number of holes in the layers close to the boundary (decreasing density) as well as in inhomogeneous distribution of end groups of n-alkanes in layers (there are more of them in the first layer). Changes in surface tension of n-alkanes with the increase in molecule chain length or temperature correlate with the change of variables that describe concentration and orientation inhomogeneities of the surface layer.

The obtained density profile of the surface layer of n-alkanes and CH₃- group behaviour of n-alkane molecules in the surface area that was predicted by the calculations comply with the findings of other authors who used molecular dynamics methods (14) and a gradient theory (15).

It is impossible nowadays to experimentally determine the density profile of the surface layer of liquids. However, to be able to explain temperature and concentration dependences of the character of the surface layer of pure liquids and their mixtures, e.g. n-alkanes, one needs to know the character of the dependence of the surface area density on the coordinate of the normal to the surface of the liquid-vapor interface. According to the latticed model vacancies (16), the lattice place ν_0 is considered to be unchanged for the whole system, no matter what temperature and composition it has. To calculate the volume $V^{(p)}$ of the p-layer of the surface layer the following formula can be used

$$V^{(p)} = \nu_0 N_A^{(p)} r / \varphi_A^{(p)}, \quad (1)$$

where $N_A^{(p)}$ is the number of molecules of an r-mer in a layer; r – the number of places occupied by an r-mer in the lattice.

The p-layer density is equal to

$$\rho^{(p)} = \rho^* \cdot \varphi_A^{(p)}, \quad (2)$$

where $\rho^* = \mu / r\nu_0$ - density of a tightly packed system (without holes); μ - molar weight.

$$\rho^{(p)} = \frac{\mu}{r\nu_0} \cdot \varphi_A^{(p)}. \quad (3)$$

So, to calculate the density of the p-layer of the impure phase, the following formula can be used

$$\rho^{(p)} = \frac{\mu}{r\nu_0} \cdot \varphi_A^{(p)}. \quad (3)$$

Formula (3) can also be used for r-mer mixtures. Accordingly, the density of the layer of the surface area is determined by the volumetric part of the molecules of an r-mer φ_A (r-mers) in layer p (16). Table 3 and article (9) show the density of a tightly packed system for pure n-alkanes. The obtained results (Fig. 3) to those of the alike research carried out with the help of the gradient theory (14) and methods of molecular dynamics (15).

Table 3: Density of a tightly packed system for pure n-alkanes (C_n – number of the C-atoms in the molecular chain of n-alkanes)

C _n	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁
ρ^* , g/cm ³	0,7551	0,7868	0,8113	0,8308	0,8468	0,8600	0,8712
C _n	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇	C ₁₈
ρ^* , g/cm ³	0,8807	0,8890	0,8962	0,9026	0,9082	0,9132	0,9178

Density, g/cm³

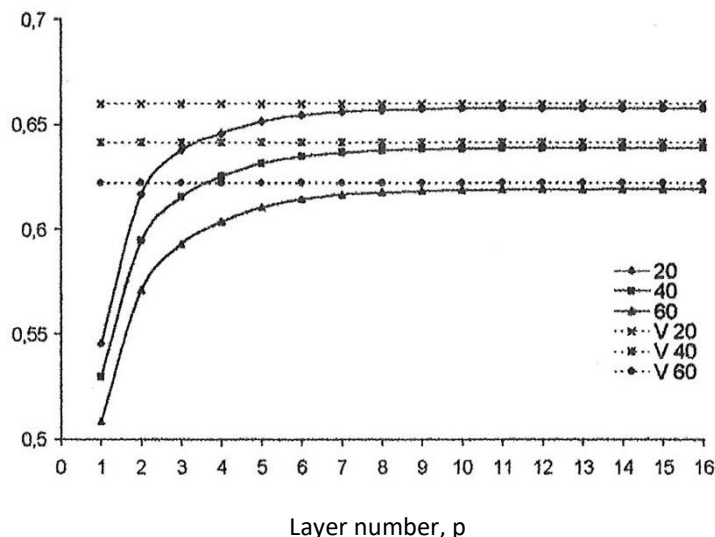


Fig 3: Density profiles of the surface area of hexane at 20°C, 40°C and 60°C; p – layer number; horizontal lines – densities of the volume phase at certain temperatures.

CONCLUSION

As calculations show, in terms of their structure, density and orientation inhomogeneity, it is only the first 2-3 layers that are very different from the volume phase. So, it is possible to make an introductory conclusion that a relatively small surface area plays a crucial role in the formation of surface properties and processes in systems resembling those of n-paraffin. A mechanism of the surface tension in such systems is built into the structure of that area and behaviour of the r-mer chain links.

REFERENCES

- [1] Smirnova, N.A. (1973). Application of the multilayer model of the lattice to study the concentration and orientational heterogeneity of the solution near the flat boundary surface. *Colloid journal*, 35(6), 1090-1099.
- [2] Smirnova, N.A. (1977). Multilayer lattice model for studying the surface properties of a monomer-dimer solution with directed intermolecular interactions. General equations in the case of a symmetric dimer. *Colloid journal*; 39(6), 92-99.
- [3] Smirnova, N. A.(1979). Model of the surface layer of a multicomponent solution formed by molecules of similar size. *Colloid journal*; 41(6), 1152-1156.
- [4] Smirnova, N. A. (1980). Lattice model of the surface layer of a solution containing r-measures with links of arbitrary type. 1. Description of models and the derivation of general relations. *Colloid journal*; 42(1), 84-90.
- [5] Barker, J.A. (1963). *Lattice theories of the liquid state*. New York, NY.
- [6] Dozorov, V. A. (1997). Independent variables in the statistical sum for the surface phase of a multilayer lattice model of n-alkane solutions. *Fundamental and applied research*, 1, 75-82.
- [7] Dozorov, V. A. (1998). Experience of using a multilayer lattice model of the surface phase with vacancies to the study of the concentration and orientational inhomogeneities of pure n-alkanes near a flat boundary surface. *Fundamental and applied research*, 2, 63-74.
- [8] Dozorov, V. A.(1999). Multilayer adsorption model for monomer-r-mer systems. *Science - University - School*, 5, 316-319.
- [9] Dozorov, V. A. (2001). Calculation of the concentration and orientational heterogeneity of the surface layer of n-alkanes and their mixtures using a multilayer hole grating model. St. Petersburg. *Bulletin of SPbSU*, 4(28), 43-48.
- [10] Dozorov, V. A. (2002). Calculation of the density profile of the surface layer of n-alkanes and their mixtures. *XIV International Conference on Chemical Thermodynamics*(p 380). St. Petersburg.

- [11] Smirnova, N. A., Brodskaya, E. N.(1974). Application of the multilayer model of the lattice to study the concentration and orientational inhomogeneity of the solution near a flat boundary surface. Calculations for the acetone-chloroform system. *Colloid journal*,36(1), 63-70.
- [12] Smith, A.E. (1953). The Crystal structure of the normal paraffin hydrocarbons. *J. Chem. Phys*,21(12), 2229-2231.
- [13] Melnikov, G. A., Skryshevsky, A. F., Otpuschennikov, N. F.(1986). Structural characteristics of liquids with linear molecules. *The physics of the liquid state*,14, 68-76.
- [14] Kawamata, M., Yamamoto, T. (1997). Molecular dynamics simulation of surface ordering in liquid n-alkanes. *T.Phys.Society of Japan*,66(8), 2350-2354.
- [15] Cornelisse, P.M.W. (1997). *The gradient theory applied. Simultaneous modeling of interfacial tension and phase behavior*. Netherlands, Delft: Proefschrift.
- [16] Dozorov, V. A. (2001). *Surface properties of n-alkanes and their mixtures. Modeling in the framework of the lattice model. PhD thesis*. St. Petersburg,Russia.