

Quantum Chemical Analysis of the Thermodynamics of 2D Cluster Formation of Odd *n*-Alcohols at the Air/Water Interface

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Reasonable values of the thermodynamic characteristics for the cluster formation of odd alcohols at the air/water interface are obtained by the quantum chemical PM3 approximation. The calculated values of enthalpy ΔH_m^{cl} , entropy ΔS_m^{cl} and Gibbs energy ΔG_m^{cl} for the formation of clusters of a given structure depend linearly on the number of CH₂ groups in the odd alcohol molecule. The additive approach, proposed in a recent paper, was further developed to extend the results of the calculations of the thermodynamic properties of small associates (2 to 7 alcohol molecules) to infinite clusters of odd and even homologues. Hydrogen O···H bonds, O···O interactions between the oxygen lone pairs, and four types of H···H interaction are taken into account, and the thermodynamic characteristics of the formation of linear, rhombic, rectangular, etc. clusters are calculated. Depending on the cluster type, the dependence of the Gibbs free energy on the alkyl chain length can be either the same for all homologous alcohols or can be different for the even and odd homologues. The most stable associates are clusters possessing rhombic or dodecahedral structures and linear clusters possessing one H···H bond per each methylene group. The former type exhibits a monotonic dependence of the thermodynamic parameters on the number of methylene groups, whereas for the latter type this dependence is stepwise. The results of the quantum chemical calculations agree well with the results obtained on the basis of a thermodynamic model that assumes equilibrium between oligomers and clusters within the monolayer. The experimental Π -A isotherms, indicating the existence of a first-order phase transition, and the microscopic morphology of the condensed-phase domains of tridecanol monolayers support the results of the quantum chemical and thermodynamic calculations.

Introduction

In our recent studies,^{1–3} the enthalpy ΔH_m^{cl} , entropy ΔS_m^{cl} , and Gibbs energy ΔG_m^{cl} of dimerization and clusterization ($m = 2–7$) were calculated using the PM3 method for the nonbranched fatty alcohols with even numbers of carbon atoms ($n = 8–16$). The results of the calculations of thermodynamic functions performed for finite associates were extrapolated onto infinite cluster size in two different ways: (i) using exponential or hyperbolic extrapolation and (ii) assuming additivity of the thermodynamic parameters that describe the cluster formation. The additivity model implies a linear dependence of the cluster characteristics on the number of CH₂ groups in the alcohol molecule also for different structural types, taking into account the existence of hydrogen O–H bonds and assuming four different types of interactions between the alkyl chains. The results of the calculations were found to be in good agreement with the data obtained from the thermodynamic characteristics of the 2D phase transitions observed in spread and adsorbed alcohol monolayers, estimated from the experimental surface pressure–area (Π -A) isotherms using thermodynamic models.^{4,5}

The formation of the so-called H···H hydrogen bonding or dihydrogen bonding can obey either of two different mecha-

nisms.⁶ The first one, which involves the electrostatic interaction between oppositely charged hydrogen atoms and results in high bonding energy (4–30 kJ/mol), is inappropriate for the interaction of alcohol molecules, where dispersion interaction takes place between the nonpolar hydrocarbon –CH₂– fragments. For this case, the ab initio calculations⁷ have shown that a minimum exists at the intermolecular potential energy hypersurface.

In a previous publication,² we reviewed briefly the methods used to perform calculations of molecular clusters. Here we present some additional considerations. To study the clusterization of higher fatty alcohols, molecular mechanics methods (MM2, MM3, AMBER)^{8,9} and semiempirical quantum chemical methods (MINDO/3, MNDO, AM1, PM3) were generally used. Molecular mechanics methods are essentially based on empirical potential functions, either two-particle (e.g., Lennard-Jones) or multiparticle cooperative interactions.^{11–13} It should be noted that both types of methods involve parameters that are chosen from the best fit between the values calculated by the method and those obtained from ab initio calculations or the experimental data. However, the semiempirical quantum chemical methods are based on more rigorous theoretical foundations than the molecular mechanic methods. The semiempirical quantum chemical methods involve the NDDO (neglecting of diatomic differential overlapping) approximation,¹⁰ which is incapable of the correct description of the interaction between nonbonded atoms with distances close to the van der Waals radii. However,

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the introduction of different functions of the Gauss type to account for attraction and repulsion^{14,15} improved essentially the values of various physicochemical characteristics calculated using semiempirical methods. For example, the values of the formation enthalpy and internal rotation energy barriers yielded by the fully reparametrized PM3 method¹⁵ are the most correct values, as compared with those from other semiempirical methods.¹⁶ This PM3 method was successfully used to estimate the intermolecular interaction energy;^{17,18} also, it is capable of the calculation of electronic distributions and vibration frequencies and of the estimation of the entropy contributions to the association free energy.

In the present work, the results obtained earlier are complemented by the calculations performed for odd n -alcohols of the general formula $C_nH_{2n+1}OH$, where $n = 7-15$. On the basis of the analysis of the aggregation for even and odd alcohols, it became possible to modify and generalize our earlier approach to the estimation of characteristic parameters for infinite ordered clusters. By comparing the results thus obtained with the experimental values of the characteristic thermodynamic parameters for 2D phase transitions in the monolayers at the gas/liquid interface, it becomes possible to predict the morphologic structure of the clusters.

Methods

Similar to our recent publications,¹⁻³ the semiempirical calculations of the cluster formation were carried out with the MOPAC 2000 suite of programs¹⁰ using the PM3 molecular orbital approximation. The calculations for monomers and dimers were also performed using the MINDO/3, MNDO, and AM1. Full geometry optimizations were performed on single alcohol molecules and on the studied molecular complexes with the Broyden-Fletcher-Goldfarb-Shanno optimization algorithm¹⁰ because the default geometry optimizer, Eigenvector Following, is unsuitable for large systems. Standard entropy and Gibbs energy values were estimated using the usual equations of statistical thermodynamics with translational, rotational, and vibrational terms.¹⁰ It is known that for van der Waals molecules the intermolecular vibrations of low frequency ($<100\text{ cm}^{-1}$)¹⁹ are essential. It was shown in refs 1 and 2 that these vibrations are important for a correct description of the clusterization entropy and free energy. Because the recent MOPAC versions disregard the frequencies below 100 cm^{-1} , which contribute most significantly to the vibrational entropy constituent, an additional procedure was developed to take these contributions into account.

Experimental Section

The surface pressure–area (Π – A) isotherms were measured at different temperatures using a computer-interfaced film balance. The surface pressures measured with the Wilhelmy method using a roughened glass plate were reproducible to $\pm 0.1\text{ mN m}^{-1}$, and the areas per molecule, to $\pm 0.005\text{ nm}^2$. The film balance was sheltered in a cabinet to avoid excessive disturbances by convection and contamination by impurities. After the spreading solvent evaporated, the molecules remaining at the air/water interface were continuously compressed and expanded at rates of $0.002-1.35\text{ nm}^2\text{ molecule}^{-1}\text{ min}^{-1}$.

Imaging of the tridecanol monolayer was performed with a Brewster angle microscope (BAM 1+, NFT, Göttingen) mounted on the film balance. Because the BAM images are distorted due to the observation at the Brewster angle, image-processing software was used to correct the distortion of the digitized images. The lateral resolution of the BAM was approximately $4\text{ }\mu\text{m}$.

TABLE 1: Standard Enthalpy of Formation of Odd Alcohols

molecule	ΔH_{298}^0 , kJ/mol					exp
	MINDO/3	MNDO	AM1	PM3	PM3a	
CH ₃ OH	-211.95	-239.97 ^a	-238.61 ^a	-217.05 ^a	-214.60	-201.17
C ₃ H ₇ OH	-289.80	-282.91	-297.62	-268.01	-260.65	-257.53
C ₅ H ₁₁ OH	-342.17	-322.28	-354.80	-313.27	-301.01	-302.38
C ₇ H ₁₅ OH	-394.57	-361.69	-412.08	-358.61	-341.44	-334.85
C ₉ H ₁₉ OH	-446.99	-401.09	-469.38	-403.96	-381.88	-386.89
C ₁₁ H ₂₃ OH	-499.39	-440.50	-526.68	-449.32	-422.33	-422.21
C ₁₃ H ₂₇ OH	-551.81	-479.90	-583.98	-494.68	-462.79	-463.46
C ₁₅ H ₃₁ OH	-604.22	-519.31	-641.28	-540.00	-503.21	-504.67

^a Coincides with the data in ref 10.

TABLE 2: Standard Entropy of Formation of Odd Alcohols

molecule	ΔS_{298}^0 , kJ/mol					exp
	MINDO/3	MNDO	AM1	PM3	PM3a	
CH ₃ OH	238.65	238.76	238.25	238.69	245.29	239.70
C ₃ H ₇ OH	311.85	306.18	306.05	304.61	324.41	324.80
C ₅ H ₁₁ OH	382.58	372.39	372.53	369.60	402.59	400.83
C ₇ H ₁₅ OH	453.05	438.28	438.84	434.46	480.65	480.45
C ₉ H ₁₉ OH	522.44	503.18	504.43	499.12	558.50	558.35
C ₁₁ H ₂₃ OH	591.25	567.68	569.34	563.34	635.92	636.26
C ₁₃ H ₂₇ OH	659.17	630.65	634.32	627.81	713.58	712.83
C ₁₅ H ₃₁ OH	726.40	693.57	698.50	690.83	789.80	790.73

The n -alcohols and the spreading solvent n -heptane were obtained from Merck (Germany) and were used as received. The sample of n -C₁₃H₂₇OH had a nominal purity of 99+%. The subphase water was Millipore filtered. Spreading solutions of 10^{-3} M were used.

Results and Discussion

The thermodynamic parameters of the clusterization are defined as the differences between the values of enthalpy, entropy, and Gibbs energy for the clusters (subscript m) and monomers (subscript 1):

$$\begin{aligned}\Delta H_m^{\text{cl}} &= \Delta H_m - m\Delta H_1 & \Delta S_m^{\text{cl}} &= \Delta S_m - m\Delta S_1 \\ \Delta G_m^{\text{cl}} &= \Delta G_m - m\Delta G_1\end{aligned}\quad (1)$$

where m is the number of molecules in a cluster.

Thermodynamic Parameters for the Formation of n -Alcohols. The calculated values of standard thermodynamic characteristics ΔH_{298}^0 and ΔS_{298}^0 for the formation of odd alcohol monomers are shown in Tables 1 and 2; the experimental values²⁰ are also listed. It follows from the data that the semiempirical methods lead to quite poor agreement with the experimental data: the average error in the calculation of ΔH_{298}^0 is 63, 21, 89, and 23 kJ/mol for the MINDO/3, MNDO, AM1, and PM3 methods, respectively. The difference between the calculated and experimental results for alcohols is roughly proportional to the alkyl chain length. By introducing the correction per CH₂ fragment, calculated by the least-squares method, one obtains significantly lower standard deviation values for all methods except MNDO: $S_{\text{MINDO/3}} = 7.9\text{ kJ/mol}$, $S_{\text{AM1}} = 16.3\text{ kJ/mol}$, and $S_{\text{PM3}} = 3.7\text{ kJ/mol}$. The PM3 method is seen to ensure the most accurate results. The calculated formation enthalpies with the additive correction of $2.45 \pm 0.09\text{ kJ/mol}$ per methylene group are presented in Table 1 ("PM3a" column). However the systematic error of the PM3 method does not affect the calculated values of the dimerization and clusterization energies because of the reciprocal compensation.

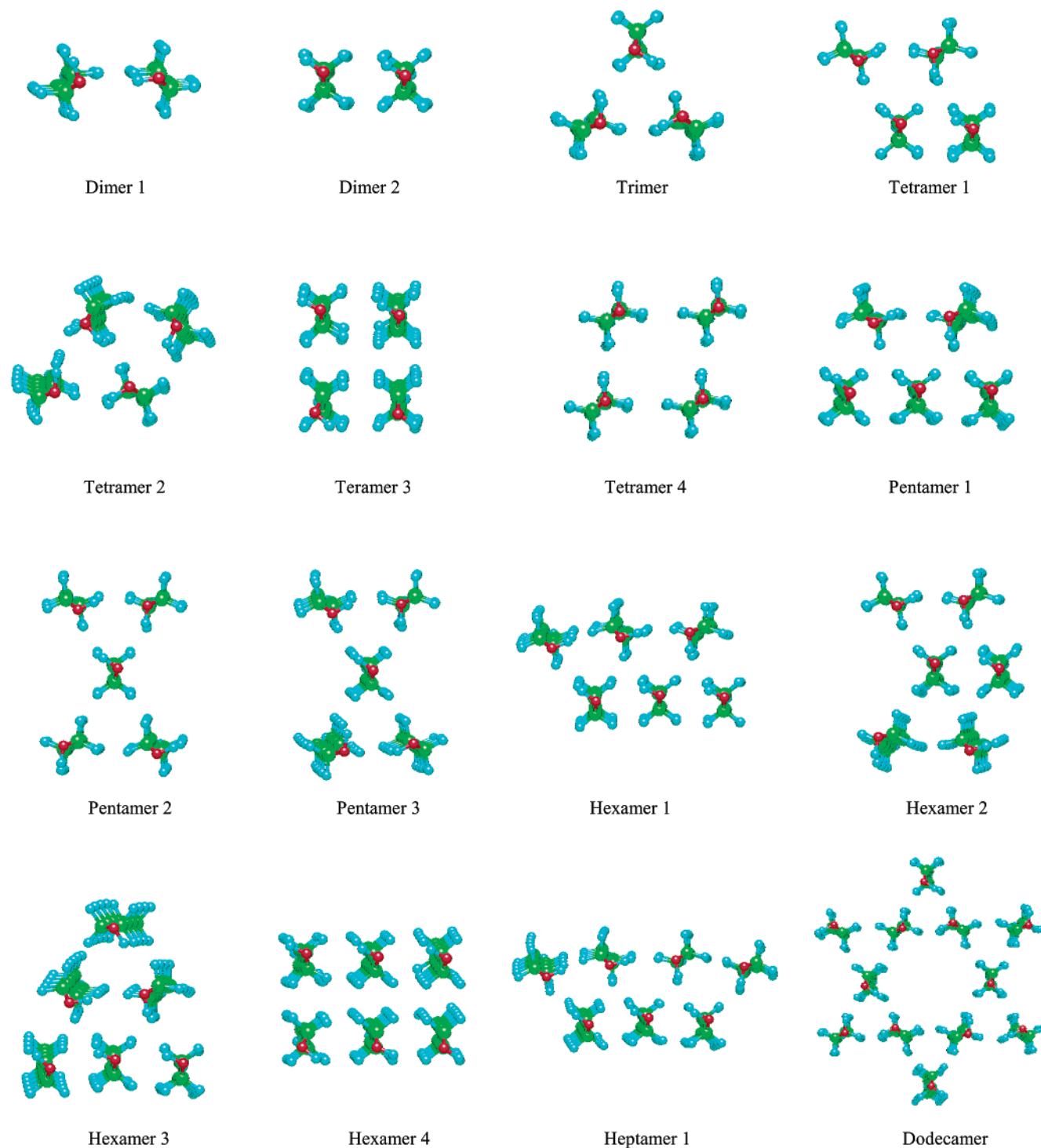


Figure 1. Different structures of alcohol clusters (schematically). For a detailed explanation, see the text.

It is seen from Table 2 that the calculated entropy values are also somewhat lower than the experimental values. This fact can be attributed to the free rotation of alkyl groups that was disregarded in the calculations. Assuming that the correction for the free rotation is also proportional to the alkyl chain length, one can account for this effect additively. This procedure leads to quite good agreement with the experiment for the four methods with the following standard deviations: $S_{\text{MINDO/3}} = 1.9$ J/mol K, $S_{\text{MNDO}} = 2.4$ J/mol K, $S_{\text{AM1}} = 1.8$ J/mol K, and $S_{\text{PM3}} = 1.8$ J/mol K. The results of these calculations for the PM3 method are presented in Table 2, ("PM3a" column).

Thermodynamic Parameters of Dimerization. The calculated conformations of dimers are shown in Figure 1, whereas the calculated results are listed in Table 3. It was shown earlier² that the PM3 method is the only semiempirical method that predicts the formation of stable dimers (i.e., it yields negative Gibbs energy values ΔG_m^{dim} for the dimerization of alcohols). It is seen from Table 3 that the ΔG_m^{dim} value becomes negative for the tridecanol conformation of Dimer 1 and becomes lower with the increase of the chain length.

It should be noted that in modeling of dimerization and clusterization, the effect of the medium was disregarded (in other

TABLE 3: Standard Thermodynamics Characteristics of Formation of Alcohol Clusters Calculated at the PM3 Approximation (ΔH and $T\Delta S$ in kJ/mol, ΔS in J/mol K)

system	ΔH_m	ΔH_m^{cl}	ΔS_m	ΔS_m^{cl}	$-T\Delta S_m^{\text{cl}}$	ΔG_m^{d}
G_m^{cl}Dimer 1						
C ₇ H ₁₅ OH	-751.141	-33.928	715.71	-153.22	45.659	11.731
C ₉ H ₁₉ OH	-852.247	-44.325	820.43	-177.80	52.984	8.659
C ₁₁ H ₂₃ OH	-953.324	-54.693	927.34	-199.33	59.402	4.708
C ₁₃ H ₂₇ OH	-1054.418	-65.053	1038.46	-217.15	64.711	-0.342
C ₁₅ H ₃₁ OH	-1155.508	-75.500	1159.98	-221.67	66.058	-9.442
Dimer 2						
C ₇ H ₁₅ OH	-763.580	-46.367	627.14	-241.78	72.052	25.685
C ₉ H ₁₉ OH	-866.603	-58.681	714.22	-284.01	84.635	25.955
C ₁₁ H ₂₃ OH	-969.650	-71.019	800.63	-326.05	97.162	26.143
C ₁₃ H ₂₇ OH	-1072.711	-83.345	887.02	-368.59	109.840	26.494
C ₁₅ H ₃₁ OH	-1175.775	-95.768	973.01	-408.65	121.777	26.009
Trimer						
C ₇ H ₁₅ OH	-1169.587	-93.768	952.21	-351.18	104.652	10884
C ₉ H ₁₉ OH	-1334.173	-122.290	1095.26	-402.09	119.824	-2.466
C ₁₁ H ₂₃ OH	-1498.784	-150.837	1237.42	-452.59	134.872	-15.965
C ₁₃ H ₂₇ OH	-1663.433	-179.385	1389.09	-494.33	147.309	-32.075
C ₁₅ H ₃₁ OH	-1828.077	-208.066	1533.57	-538.92	160.598	-47.468
Tetramer 1						
C ₇ H ₁₅ OH	-1590.548	-156.122	1101.78	-636.07	189.548	33.427
C ₉ H ₁₉ OH	-1818.212	-202.368	1258.99	-737.48	219.768	17.401
C ₁₁ H ₂₃ OH	-2045.943	-248.680	1434.13	-819.22	244.127	-4.553
C ₁₃ H ₂₇ OH ^a	-2273.690	-294.959	1575.77	-935.45	278.764	-16.195
Tetramer 2						
C ₇ H ₁₅ OH	-1590.811	-156.385	1110.31	-627.54	187.006	30.621
C ₉ H ₁₉ OH	-1817.906	-202.062	1278.06	-718.41	214.085	12.023
C ₁₁ H ₂₃ OH	-2045.030	-247.768	1446.65	-806.70	240.397	-7.371
C ₁₃ H ₂₇ OH	-2272.201	-293.470	1612.07	-899.15	267.947	-25.523
C ₁₅ H ₃₁ OH ^a	-2499.425	-339.410	1776.38	-986.94	294.108	-45.303
Tetramer 3						
C ₇ H ₁₅ OH	-1567.456	-133.030	988.03	-749.82	223.446	90.416
C ₉ H ₁₉ OH	-1784.848	-169.004	1128.19	-868.27	258.746	89.741
C ₁₁ H ₂₃ OH	-2002.123	-204.861	1270.90	-982.45	292.771	87.910
C ₁₃ H ₂₇ OH	-2219.403	-240.672	1410.49	-1100.73	328.018	87.346
Pentamer 1						
C ₇ H ₁₅ OH	-2009.358	-216.325	1272.92	-899.39	268.019	51.694
C ₉ H ₁₉ OH	-2299.869	-280.064	1459.65	-1035.93	308.707	28.643
C ₁₁ H ₂₃ OH	-2590.444	-343.866	1641.15	-1175.54	350.310	6.444
C ₁₃ H ₂₇ OH	-2881.077	-407.664	1830.37	-1308.65	389.978	-17.686
Pentamer 2						
C ₇ H ₁₅ OH	-1994.743	-201.711	1426.76	-745.56	222.175	20.465
C ₉ H ₁₉ OH	-2278.694	-258.889	1658.00	-837.58	249.600	-9.290
C ₁₁ H ₂₃ OH	-2562.687	-316.110	1897.56	-919.13	273.900	-42.209
C ₁₃ H ₂₇ OH ^a	-2846.718	-373.305	2094.87	-1044.15	311.157	-62.148
Pentamer 3						
C ₇ H ₁₅ OH	-1975.877	-182.845	1453.71	-718.60	214.143	31.298
C ₉ H ₁₉ OH	-2259.925	-240.120	1688.47	-807.12	240.521	0.402
C ₁₁ H ₂₃ OH	-2544.023	-297.445	1926.00	-890.69	265.426	-32.019
Hexamer 1						
C ₇ H ₁₅ OH	-2435.260	-283.621	1439.66	-1167.11	347.800	64.179
C ₉ H ₁₉ OH	-2791.042	-367.276	1651.43	-1343.27	400.295	33.019
C ₁₁ H ₂₃ OH	-3146.883	-450.989	1859.32	-1520.70	453.170	2.181
Hexamer 2						
C ₇ H ₁₅ OH	-2435.314	-283.675	1539.30	-1067.47	318.107	34.432
C ₉ H ₁₉ OH	-2787.703	-363.937	1769.55	-1225.15	365.094	1.158
C ₁₁ H ₂₃ OH	-3140.188	-444.295	2014.62	-1365.41	406.893	-37.402
Hexamer 3						
C ₇ H ₁₅ OH	-2431.389	-279.751	1445.17	-1161.60	346.157	66.406
C ₉ H ₁₉ OH	-2784.783	-361.016	1654.19	-1340.51	399.472	38.455
C ₁₁ H ₂₃ OH	-3138.293	-442.399	1864.59	-1515.44	451.601	9.202
Hexamer 4						
C ₇ H ₁₅ OH	-2393.867	-242.228	1310.33	-1296.44	386.340	144.111
C ₉ H ₁₉ OH	-2732.043	-308.277	1500.39	-1494.31	445.305	137.028
C ₁₁ H ₂₃ OH	-3070.182	-374.288	1692.13	-1687.90	502.994	128.706
Heptamer 1						
C ₇ H ₁₅ OH	-2856.864	-346.619	1622.27	-1418.96	422.851	76.231
C ₉ H ₁₉ OH	-3277.737	-450.010	1859.10	-1634.72	487.145	37.135
C ₁₁ H ₂₃ OH	-3698.756	-553.547	2097.99	-1845.37	549.921	-3.626

^a Presence of one small negative frequency in an oscillatory spectrum.

words, it was assumed that the molecules are located in a vacuum). Accounting for the presence of the solvent in the framework of the conductorlike screening model (COSMO)²¹ results in an additive decrease of the absolute enthalpy values (by approximately 10 kJ/mol); therefore, similar to our earlier studies,² the effect of the solvent is neglected in further calculations.

In addition to the interaction between the alkyl chains described above for Dimer 1, another type of bonding is also possible, as shown in Figure 1 for Dimer 2. It is seen from Table 3 that Dimer 2 is characterized by a deeper minimum of the electronic energy, and the increase in the depth of this minimum with an increase of the hydrocarbon chain length is somewhat more significant than that for Dimer 1. In addition to the enthalpy, the thermodynamic stability of a dimer is also determined by the entropy factor. Higher values of the intermolecular interactions lead usually to the formation of bonded complexes with more hindered intermolecular motion.²² Therefore, the contribution from the entropy variation results in a decrease of the stability of the formed complexes. The translational and rotational contributions to the entropy for Dimers 1 and 2 are roughly equal to each other. However, because the frequency of the intermolecular vibrations for Dimer 1 is lower than that for Dimer 2, the vibration constituent for Dimer 1 is 90–180 J/(mol K) higher than that for Dimer 2. The mutual enthalpy–entropy compensation for Dimer 2 results in the fact that for all the alcohols studied the Gibbs energy values are positive and roughly equal to each other.

Similar to the even alcohols considered in ref 2, the dimers of odd alcohols demonstrate a linear dependence of the enthalpies and entropies of dimerization on the number of carbon atoms. For Dimer 1,

$$\Delta H_m^{\text{dim}} = (2.430 \pm 0.047) - (5.194 \pm 0.004)n \text{ kJ/mol}$$

$$(R = 0.999; S = 0.026 \text{ kJ/mol})$$

$$\Delta S_m^{\text{dim}} = -(96.90 \pm 12.7) - (8.81 \pm 1.11)n \text{ J/mol K}$$

$$(R = 0.980; S = 7.04 \text{ J/mol K}) \quad (2)$$

and for Dimer 2,

$$\Delta H_m^{\text{dim}} = -(3.130 \pm 0.064) - (6.173 \pm 0.006)n \text{ kJ/mol}$$

$$(R = 0.999; S = 0.036 \text{ kJ/mol})$$

$$\Delta S_m^{\text{dim}} = -(95.74 \pm 1.38) - (20.92 \pm 0.12)n \text{ J/mol K}$$

$$(R = 0.999; S = 0.77 \text{ J/mol K}) \quad (3)$$

By comparing the regression coefficients of eqs 2 and 3 with the corresponding values for even alcohols,² one can see that these values are almost equal, except for the free terms of regression 2. Therefore, for Dimer 2, the equations for both even and odd alcohols can be expressed by a single regression:

$$\Delta H_m^{\text{dim}} = -(3.167 \pm 0.039) - (6.169 \pm 0.003)n \text{ kJ/mol}$$

$$(R = 0.999; S = 0.030 \text{ kJ/mol})$$

$$\Delta S_m^{\text{dim}} = -(97.96 \pm 1.36) - (20.68 \pm 0.11)n \text{ J/mol K}$$

$$(R = 0.999; S = 1.04 \text{ J/mol K}) \quad (4)$$

For Dimer 1, the situation is different. The parameters for systems with even and odd CH₂ group numbers in the monomer are fitted by two different lines. The dimerization parameters for aggregates with odd alcohols are close to those that are characteristic for the nearest lower even homologue. Therefore, the general relations for Dimer 1 of both even and odd alcohols

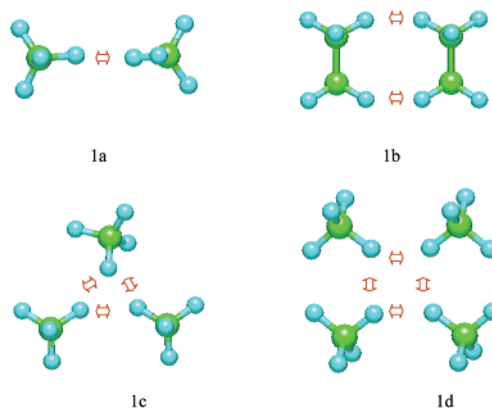


Figure 2. Various types of interactions between hydrogen atoms of alkyl chains.

can be expressed as

$$\Delta H_m^{\text{dim}} = -(2.874 \pm 0.404) - (5.154 \pm 0.035)\{n/2\}$$

$$\text{kJ/mol} \quad (R = 0.999; S = 0.337 \text{ kJ/mol})$$

$$\Delta S_m^{\text{dim}} = -(105.39 \pm 5.57) - (8.93 \pm 0.49)\{n/2\}$$

$$\text{J/mol K} \quad (R = 0.988; S = 4.63 \text{ J/mol K}) \quad (5)$$

where the symbol $\{\dots\}$ denotes the integral part of a number. These regularities can be explained by the fact that the main contribution to the interaction energy is brought by the nearest H...H contacts. In fact, the dihydrogen bonding number in Dimer 2 is exactly equal to the number of CH₂ groups, whereas in Dimer 1 these contacts exist only for even carbon atoms.

Thermodynamic Parameters of Clusterization. The geometry of clusters calculated in the study, which comprise 3 to 7 alcohol molecules ($m = 3-7$), is shown in Figure 1, whereas Table 3 summarizes the corresponding values of the enthalpy and entropy of the cluster formation and the thermodynamic parameters of the cluster formation calculated per alcohol molecule. For the tetramers and higher-order aggregates, some structures were calculated, of which the most important are the close-packed compact type 1 structures and the most loosely packed starlike type 2 structures. Whereas for the former type the maximum enthalpy decreases and a significant decrease in the oligomerization entropy takes place, for the latter, the enthalpy values are quite moderate, and the oligomerization entropy is minimal. Note that all the structures considered, if not explicitly indicated otherwise, do not possess any negative frequency values in the Hessian matrix and correspond to the minimim points on the potential energy hypersurface.

It is seen from the calculations that the most stable small aggregates are the trimers. Trimers are formed for nonanol, whereas dimers become stable ($\Delta G_m^{\text{cl}} < 0$) for dodecanol and above. It should be noted that the formation of nonanol trimers can explain the experimental surface tension isotherms reported in ref 23.

To generalize the results of the calculations, four types of H...H interaction can be distinguished. These types are shown schematically in Figure 2. The incorporation of an extra molecule into a trimer can be performed in two ways, either by a single unary H–H bonding as in Figure 2a, which leads to the structure of Tetramer 2 (see Figure 1) or by triple H–H contacts as in Figure 2c, which results in the structure of Tetramer 1. The structures of Tetramer 3 and Hexamer 4 possess the most close cubic packing, with four contacts existing between the hydrogen atoms, as shown in Figure 3d. This type

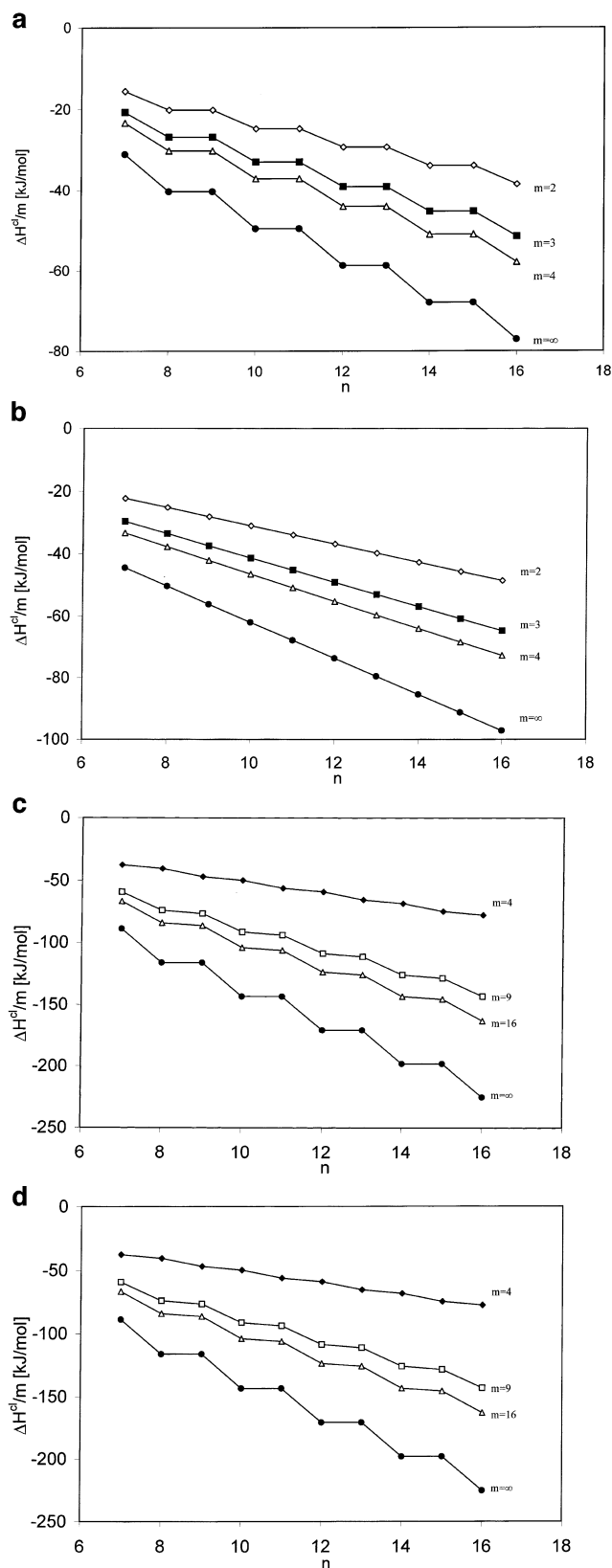


Figure 3. Dependence of the clusterization enthalpy per monomer on the number of molecules in a cluster m and the number of CH_2 groups in the monomer: (a) Dimer 1; (b) Dimer 2; (c) Tetramer; (d) Dodecamer.

of bonding does not result in the formation of clusters for any n values (see Table 3). The incorporation of one, two, etc. molecules into Tetramer 1 results in the formation of oligomers of the corresponding type 1, with enthalpies and entropies for

the clusterization per monomer ($\Delta H_m^{\text{cl}}/m$ and $\Delta S_m^{\text{cl}}/m$) being quite well described by a hyperbolic dependence on the number of molecules in the cluster.³

It also follows from Table 3 that in contrast to the monomers, for most of the complexes the thermodynamic parameters do not exhibit any common dependence on n , whereas for the even and odd alcohols, taken separately, such a dependence exists. This fact can be ascribed to the different number of H–H contacts of a certain type between the even and odd positions of hydrogen atoms in the alcohol molecule. For example, in the trimer, the number of H–H interactions in the even position of the chain is three, whereas in the odd position this number is zero so that the trimerization parameters for the even alcohols are close to that for the next-higher odd alcohols. In Pentamer 2, the number of dihydrogen bonds for even and odd positions of hydrogen atoms is the same. At the same time, for Pentamer 3, the number of immediate H–H contacts in even alcohols is by 6 larger than that for the corresponding odd alcohol. Therefore, the odd clusters of the Pentamer 2 structure are more stable and the even clusters of the Pentamer 3 structure are less stable than those of the Pentamer 3 structure.

It has recently been shown² that the calculated ΔH_m^{cl} and ΔS_m^{cl} values for the clusters of even alcohols can be satisfactorily described by linear dependencies on the number of CH_2 groups in a monomer, with the free terms and coefficients of these dependencies being expressed by the values of certain interaction types between the polar OH groups and hydrocarbon tails, respectively. A similar procedure performed for odd alcohols yields virtually the same slope values. However, the free terms of the regressions cannot be expressed in terms of the interaction between the polar headgroups in the clusters because the n dependencies for the even and odd positions of hydrogen atoms are not the same. Therefore, in the present study, we assume that the clusterization energy (and the entropy) can be separated into the contributions from pair interactions between the hydrogen atoms, which are additive and independent of each other. For any structure of a given cluster, the number of $\text{O}\cdots\text{O}$ interactions between the lone pairs of oxygen atoms and four types of $\text{H}\cdots\text{H}$ interactions shown in Figure 2 (pair H–H interactions are indicated by arrows) can be determined on the basis of hydrogen $\text{O}\cdots\text{H}$ bonds.

From the values of the entropy and enthalpy for the cluster formation of even and odd n -alkanols (a total of 101 clusters were calculated), the following correlation equations were obtained:

$$\begin{aligned} \Delta H_m^{\text{cl}} = & -(3.49 \pm 0.54)n_{\text{O-H}} - (9.20 \pm 0.08)k_a - \\ & (5.85 \pm 0.15)k_b - \\ & (6.88 \pm 0.08)k_c - (3.41 \pm 0.11)k_d \\ & (R = 0.999; S = 6.09 \text{ kJ/mol}) \\ \Delta S_m^{\text{cl}} = & -(72.4 \pm 3.3)n_{\text{O-H}} - (55.8 \pm 5.0)n_{\text{O-O}} - (18.4 \pm \\ & 0.6)k_a - (20.4 \pm 0.9)k_b - \\ & (14.0 \pm 0.6)k_c - (12.5 \pm 0.8)k_d \\ & (R = 0.997; S = 36.1 \text{ J/(mol K)}) \quad (6) \end{aligned}$$

where $n_{\text{O-H}}$, $n_{\text{O-O}}$, k_a , k_b , k_c , and k_d are the numbers of O–H, O–O, and H–H contacts between the hydrogen atoms of alkyl groups. Note that according to the notation used in Figure 2 the a, b, c, and d interactions correspond to 1, 2, 3, and 4 contacts, respectively. The correlation relations involve only clusters that do not exhibit negative vibrational frequencies. The

additive parameters for the interaction of alkyl groups calculated in this way were found to be quite similar to the interaction parameters averaged per CH₂ group, as obtained in ref 2, with interactions of types a and c corresponding to the positive ($\Delta G < 0$) contributions and interactions of types b and d corresponding to the negative ($\Delta G > 0$) contributions to the thermodynamic stability of the cluster.

The additive scheme of the calculation of ΔH_m^{cl} and ΔS_m^{cl} can be applied to clusters of any size, including the infinite clusters. To perform the calculation, one has to account for all types of intermolecular interactions in the cluster and apply the correlation equations (eq 6).

Consider first the structures of linear chains formed in a regular order on the basis of the structure of Dimer 1. Here the numbers of interactions of various types per monomer are

$$k_a = \{n/2\}(m-1)/m \quad k_b = k_c = k_d = n_{\text{O-O}} = 0 \\ n_{\text{O-H}} = (m-1)/m \quad (7)$$

where m is the number of monomers in the cluster. In the limiting case of an infinite cluster $m \rightarrow \infty$, one obtains $k_{a\infty} = \{n/2\}$, $n_{\text{O-H}\infty} = 1$. Then for standard conditions, $\Delta H_{\infty}^{\text{cl}} = -3.49 - 9.20\{n/2\}$ kJ/mol, $\Delta S_{\infty}^{\text{cl}} = -72.38 - 18.42\{n/2\}$ J/(mol K), and $\Delta G_{\infty}^{\text{cl}} = 18.08 - 3.71\{n/2\}$ kJ/mol. Therefore, for octanol and nonanol, $\Delta G_{\infty}^{\text{cl}} > 0$ and clusters are not formed; for decanol and undecanol, $\Delta G_{\infty}^{\text{cl}} \approx 0$, whereas for dodecanol and higher homologues, $\Delta G_{\infty}^{\text{cl}} < 0$, corresponding to the formation of stable infinite clusters.

For infinite regular chains built on the basis of the structure of Dimer 2, the number of interactions per monomer is $k_{b\infty} = n$, $k_{a\infty} = k_{c\infty} = k_{d\infty} = n_{\text{O-O}\infty} = 0$, $n_{\text{O-H}\infty} = 1$. Then, under standard conditions, $\Delta H_{\infty}^{\text{cl}} = -3.49 - 5.85n$ kJ/mol, $\Delta S_{\infty}^{\text{cl}} = -72.38 - 20.41n$ J/(mol K), and $\Delta G_{\infty}^{\text{cl}} = 18.08 + 0.23n$ kJ/mol. It is seen that for any n value the formation of stable clusters is impossible.

For infinite rhombic clusters, the structural unit is Tetramer 4, for which $k_a = 2n$, $k_b = k_c = k_d = 0$, $n_{\text{O-H}} = n_{\text{O-O}} = 2$. In the general case of the 2D m cluster with the side of the rhombus composed of p monomers ($p^2 = m$), the parameter values per monomer are

$$k_a = 2n(1 + 2 + \dots + p - 1)/p^2 = n(p-1)/p \\ k_b = k_c = k_d = 0 \quad n_{\text{O-H}} = n_{\text{O-O}} = (p-1)/p \quad (8)$$

which in the $p \rightarrow \infty$ limit become $k_{a\infty} = n$, $k_{b\infty} = k_{c\infty} = k_{d\infty} = 0$, $n_{\text{O-H}\infty} = n_{\text{O-O}\infty} = 1$. In this case, one obtains $\Delta H_{\infty}^{\text{cl}} = -3.49 - 9.20n$ kJ/mol, $\Delta S_{\infty}^{\text{cl}} = -128.13 - 18.42n$ J/(mol K), and $\Delta G_{\infty}^{\text{cl}} = 34.70 - 3.71n$ kJ/mol. For decanol, it results the value $\Delta G_{\infty}^{\text{cl}} = -2.40$ kJ/mol, indicating that the formation of clusters with such a structure is possible for dodecanol and the other higher homologues. Note that in this case and in contrast to the linear clusters formed on the basis of the structure of Dimer 1 the values of the cluster-formation parameters are exactly intermediate with respect to the corresponding values for even alcohols.

Consider next the most closely packed rectangular clusters formed on the basis of the expansion of the Dimer 2 structure in both dimensions. For the 2D cluster composed of $m = p^2$ molecules, one obtains

$$k_b = 2n(p-1)/p^2 \quad k_d = 4\{(n+1)/2\}(p-1)^2/p^2 \\ n_{\text{O-H}} = 2(p-1)/p \quad k_a = k_c = n_{\text{O-O}} = 0 \quad (9)$$

In the limit of $p \rightarrow \infty$, eqs 9 yield the parameter values $k_{d\infty} = 4\{(n+1)/2\}$ and $n_{\text{O-H}\infty} = 2$, which lead to $\Delta H_{\infty}^{\text{cl}} = -6.98 - 13.64\{(n+1)/2\}$ kJ/mol, $\Delta S_{\infty}^{\text{cl}} = -144.76 - 49.80\{(n+1)/2\}$ J/(mol K), and $\Delta G_{\infty}^{\text{cl}} = 36.16 + 1.20\{(n+1)/2\}$ kJ/mol. Similar to the case of closely packed 1D clusters, the $\Delta G_{\infty}^{\text{cl}}$ values are positive for any n .

Consider finally the less closely packed structures, which possess large lacunas in the centers of hexagons, formed from the Trimer structure. For example, for dodecanol shown in Figure 1, we have $k_a = 9n$, $n_{\text{O-H}} = n_{\text{O-O}} = 9$, and $k_b = k_c = k_d = 0$; therefore, $\Delta H_{\infty}^{\text{cl}} = -31.41 - 82.80n$ kJ/mol, $\Delta S_{\infty}^{\text{cl}} = -1153.17 - 165.78n$ J/(mol K), and $\Delta G_{\infty}^{\text{cl}} = 312.23 - 33.40n$ kJ/mol. By adding an extra coordination layer around this structure, one can see that the 42-mer with the hexagonal structure is formed in this way with $k_a = 36n$, $n_{\text{O-H}} = n_{\text{O-O}} = 36$, and $k_b = k_c = k_d = 0$. In the general case, for the cluster with the coordination number q , which comprises $m = 3q(1 + 3q)$ molecules, the number of bonds per monomer is

$$k_a = \left(\frac{n}{2}\right) \frac{18q + 36(1 + 2 + \dots + q - 1)}{12q + 18(1 + 2 + \dots + q - 1)} \equiv n(1 - 1/(3q + 1)) \\ n_{\text{O-H}} = n_{\text{O-O}} = (1 - 1/(3q + 1)) \quad (10)$$

which in the limit $q \rightarrow \infty$ yields $k_{a\infty} = n$, $k_{b\infty} = k_{c\infty} = k_{d\infty} = 0$, and $n_{\text{O-H}\infty} = n_{\text{O-O}\infty} = 1$ (i.e., the same values as were obtained for infinite rhombic clusters on the basis of the Tetramer 4 structure (see eq 8)).

The dependencies of the cluster formation enthalpy per monomer on the number of molecules in the dimer or cluster m and the number of CH₂ groups in the monomer n , calculated according to the additive approach described above, are shown in Figure 3. It is necessary to note that the parameters of the dimer obtained from eqs 6 is a little different from the values given in Table 3 but are within the limits of the calculation errors. For the clusters obtained on the basis of Dimer 1 (unlike those for Dimer 2), the steplike dependence on n is clearly seen to exist. For Dimer 2 and for clusters obtained on the basis of Dodecamer (or Tetramer 4 if $m = \infty$), the enthalpies corresponding to both even and odd n for the same m are located on the same straight line (cf. Figure 2d). The higher m is, the higher the slope of this straight line. For the dense clusters shown in Figure 3c, where b- and d-type contacts exist (see Figure 2), the dependence on n , which is almost linear for low cluster size, becomes steplike gradually with an increase in the cluster size. The dependencies of entropy for the cluster formation exhibit similar behavior.

Figure 4 illustrates the dependence of the Gibbs cluster-formation energy per monomer on the number of molecules in the dimer or cluster m and on the number of CH₂ groups in the monomer n . For Dimer 2, the ΔG_m^{cl} value is almost independent of n , whereas for dense clusters this value increases slightly with the increase in n . This value also increases for larger clusters. For loose structures formed on the basis of dodecanol (or Tetramer 4) and for linear structures formed on the basis of Dimer 1, a decrease of ΔG_m^{cl} with an increase of m is observed, accompanied by an increase in the slope of the ΔG_m^{cl} dependence on n (see Figures 4a and d). For linear Dimer 2 and for dense clusters formed on the basis of Tetramer 3, the Gibbs energies are positive, indicating that these formations are not stable. At the same time, for clusters formed on the basis of Dimer 1 and the starlike (Dodecamer) or rhombic (Tetramer 4) structures, the Gibbs energy becomes negative for $n > 9$.

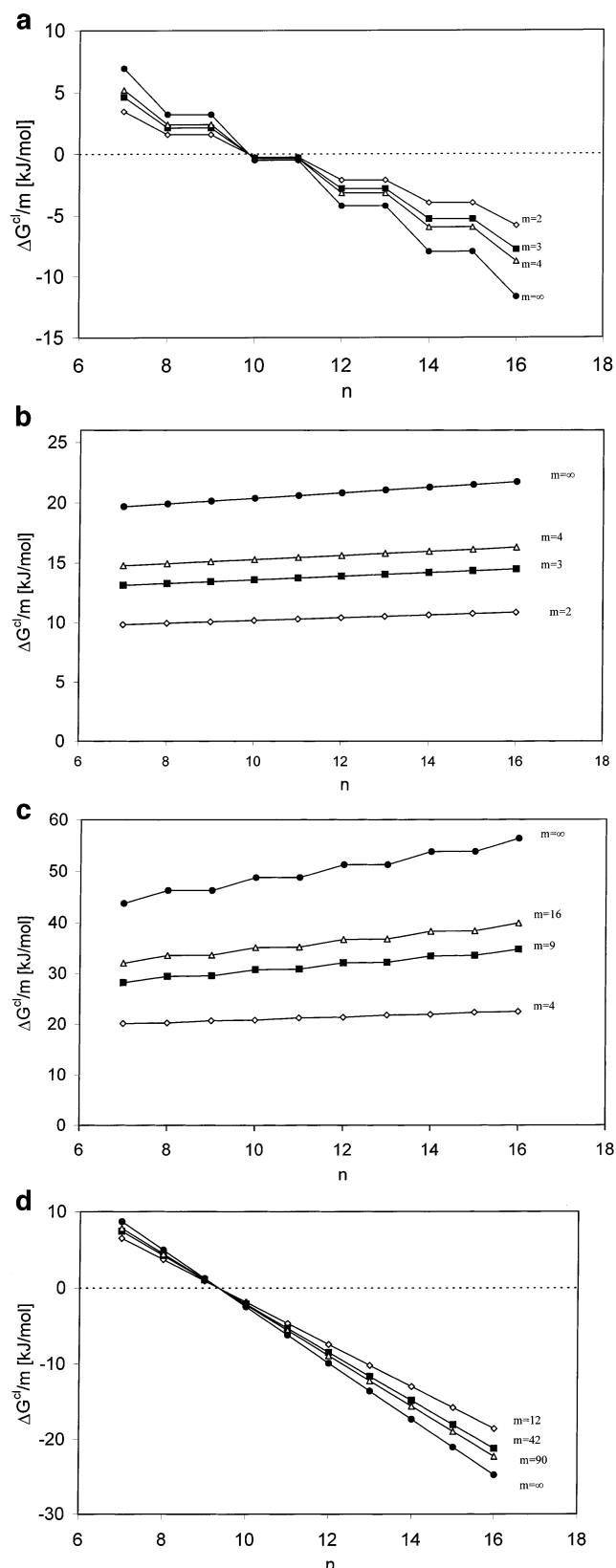


Figure 4. Dependence of the Gibbs energy for clusterization per monomer on the number of molecules in a cluster m and the number of CH_2 groups in the monomer: (a) Dimer 1; (b) Dimer 2; (c) Tetramer; (d) Dodecamer.

Starting from decanol, the Gibbs energy of the cluster formation decreases with an increase in the cluster size. This indicates that the aggregation process takes place in favor of an increase of the cluster size.

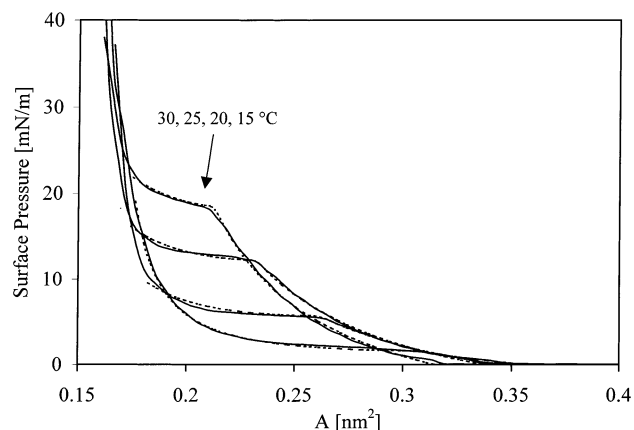


Figure 5. Experimental (solid curves) and theoretical (dashed curves) Π – A isotherms for $n\text{-C}_{13}\text{OH}$ monolayers at $T = 15, 20, 25,$ and 30 °C. The calculated parameters are given in Table 5.

TABLE 4: Parameters of the Equation of State for $n\text{-C}_{13}\text{OH}$ in a Spread Monolayer and Thermodynamic Characteristics for the Cluster Formation Out of Oligomers

temperature, °C	15	20	25	30
ω_1 , nm ²	0.16	0.16	0.16	0.16
A_c , nm ²	0.3075	0.2615	0.2325	0.2125
ϵ	0.0	0.16	0.23	0.25
m_s	4.25	3.16	2.75	2.85
ΔG^0 , kJ/mol	−1.56	−1.20	−0.93	−0.715
ΔH^0 , kJ/mol		−20.9	−15.9	−12.9
ΔS^0 , J/mol K		−67.2	−50.3	−40.3

Therefore, at the water/air interface, the formation of rhombic or starlike clusters is most probable. Also, linear clusters formed on the basis of Dimer 1 can develop. However, the Gibbs energy for stable linear chains is lower (by the absolute value) than that for rhombic or starlike clusters.

Comparison with Experiments. The experimental Π – A isotherms of tridecanol ($n\text{-C}_{13}\text{OH}$) monolayers at 15, 20, 25, and 30 °C are presented in Figure 5. From these dependencies, the thermodynamic characteristics of the transformation of small oligomers (dimers, trimers, etc.) to infinite clusters were calculated using the known thermodynamic relations presented in refs 2 and 5. Also, the experimental Π – A isotherms were compared with the theoretical isotherms calculated from the model developed in refs 2 and 4. Table 4 summarizes the thermodynamic characteristics of the aggregation process from $n\text{-C}_{13}\text{OH}$ oligomers. In Table 4, the values of the model^{2,4} parameters used to calculate the theoretical isotherms shown in Figure 5 are also presented. Here, ω_1 is the partial molecular area for monomers, A is the area per molecule, m_s is the aggregation number for small aggregates, $\epsilon = 1 - \omega_n/m\omega_1$, $\omega_n/m = \omega_{(m)}$ is the area per monomer in a cluster, and A_c is the molecular area that corresponds to the point of the commencement of the phase transition. Similar to the results obtained in ref 2 for the even homologues of alcohols, one can also see perfect agreement between the theoretical model and experimental Π – A curves for $n\text{-C}_{13}\text{OH}$. Note that according to Table 4 the tridecanol clusters are formed from tetramers or trimers and the degree of the primary oligomerization becomes lower with an increase of temperature. It was shown in ref 2 that in the dilute alcohol monolayers small oligomers are preferentially formed that can be ascribed to a relatively lower decrease in the total entropy of the system, as compared with the formation of large clusters. For large clusters, the entropy contribution to the Gibbs energy is ~ 2 kJ/mol.

The results for $n\text{-C}_{12}\text{OH}$ and $n\text{-C}_{14}\text{OH}$, which are similar to those shown in Table 4 for $n\text{-C}_{13}\text{OH}$, were presented in ref 2.



Figure 6. Characteristic domain structure of tridecanol monolayers obtained during the growth kinetics (from left to right) in the plateau region of the Π -A isotherm at 18 °C.

TABLE 5: Differences in the Thermodynamic Characteristics of Clusterization between n -C₁₃OH and n -C₁₂OH ($\Delta_{13/12}$) and between n -C₁₄OH and n -C₁₃OH ($\Delta_{14/13}$)

parameter	($\Delta_{13/12}$)	($\Delta_{14/13}$)
ΔG^0 , kJ/mol	-0.31	-0.74
ΔH^0 , kJ/mol	-2.3	-7.3
ΔS^0 , J/mol·K	-8.2	-19.7

It is interesting to analyze the differences in the thermodynamic parameters of clusterization for n -C₁₃OH as compared to that for n -C₁₂OH ($\Delta_{13/12}$) and for n -C₁₄OH as compared to that for n -C₁₃OH ($\Delta_{14/13}$). It is seen from the differences between the values of the corresponding parameters listed in Table 5 that the characteristics of the n -C₁₃OH homologue are not exactly intermediate between the adjacent even homologues but are closer to those corresponding to n -C₁₂OH: the difference between these thermodynamic values and those of n -C₁₂OH is ca. 30%, whereas with respect to n -C₁₄OH the difference is ca. 70%. By comparing these data with the quantum chemical results, one can conclude that the clusterization can lead to the formation of not only the most stable rhombic clusters but also linear structures based on Dimer 1, which may be the elements of the primary dendrite structure. Also, the defects in the infinite rhombic structure can occur because of the inclusion of admixed fragments with ΔG_m^{cl} values that are linearly dependent on $\{n/2\}$ (e.g., trimers). This conclusion is supported by the studies of n -C₁₃OH monolayers by BAM. Figure 6 shows condensed-phase domains of tridecanol monolayers grown in the "plateau" region of the Π -A isotherms at 18 °C. Three selected steps of the growth kinetics demonstrate that starting from a nearly circular compact center, dendritic arms grow in all directions around the center. Whereas at the growth the size of the circular center remains nearly unchanged, the dendritic arms become increasingly branched, starting with the unbranched linear main axes. The stable clusters of rhombic and linear structures may be the elements of the long-range orientational ordering in the microscopic domain structure in the form of the compact core and the linear elements of the dendrites.

Conclusions

The quantum chemical PM3 approximation provides reasonable values for the thermodynamic characteristics for the cluster formation of odd alcohols at the air/water interface. For a given cluster structure, the calculated values of enthalpy ΔH_m^{cl} , entropy ΔS_m^{cl} and Gibbs energy ΔG_m^{cl} for the cluster formation can be represented satisfactorily by a linear dependence on the number of CH₂ groups in the odd alcohol molecule. To extend

the results of the calculations of the thermodynamic properties of small associates (2 to 7 alcohol molecules) to infinite clusters formed by odd and even homologues, the additive approach, first proposed in ref 2, was developed further. Similar to that in the earlier studies, a linear dependence of the cluster characteristics on the number of CH₂ groups in the alcohol molecule was assumed, and hydrogen O···H bonds and O···O interactions between the oxygen lone pairs were taken into account. However, instead of distinguishing between the four types of interactions between the alkyl chains, in the present study, the four types of H···H interactions were taken into account. This method was used to calculate the thermodynamic characteristics of the clusterization for the various structures of associates: linear, rhombic, rectangular, etc. It can be shown that, depending on the structure type, the dependence of the Gibbs free energy on the alkyl chain length can be either the same for all homologous alcohols or can be different for the even and odd homologues. It was shown that the most stable associates are clusters possessing rhombic or dodecahedral structures but also linear clusters possessing one H···H bond per methylene group. The former type exhibits a monotonic dependence of the thermodynamic parameters on the number of methylene groups, whereas for the latter type this dependence is stepwise.

The experimental Π -A isotherms of n -C₁₃OH indicate the existence of a first-order phase transition in the monolayer. A thermodynamic model that assumes equilibrium between oligomers and clusters within the monolayer agrees well with the experimental results. The data obtained in these experiments are in qualitative agreement with the results of the quantum chemical calculations, both concerning the character of the dependence of the thermodynamic clusterization characteristics on the number of methylene groups and with respect to the morphological cluster structure.

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