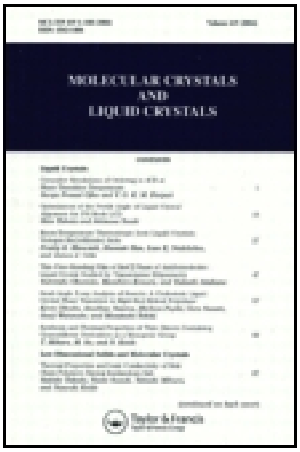

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Surface Phenomena of Liquid Crystalline Substances

– Temperature Dependence of Surface Tension of 4,4′-di-*n*-undecanoyloxybiphenyl –

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The surface tension of 4,4′-di-*n*-undecanoyloxybiphenyl has been determined as a function of temperature. A distinct deviation of its temperature dependence from the normal behavior was observed below a certain inversion temperature. The surface tension of the isotropic sample decreases sharply as the falling temperature approaches the underlying bulk phase transition point. The formation of some highly ordered structures at the liquid surface is revealed, which is consistent with the suggestion that the existence of an underlying highly ordered phase favors the pretransitional surface ordering of molecules at the free surface of an isotropic phase.

Keywords: Surface tension; temperature dependence of surface tension; anomaly in surface tension–temperature dependence; pretransitional order; surface phenomena; liquid crystals; 4,4′-di-*n*-undecanoyloxybiphenyl; 4,4′-di-*n*-alkanoyloxybiphenyls

INTRODUCTION

The dependence of surface tension on temperature ($\gamma(T)$-curve) may be described by the Eötvös-relation [1] for almost all ordinary liquids. This relation states that the surface tension increases monotonously, nearly

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linearly with decreasing temperature. However, there have been reports on anomalies of this behavior for some liquids and especially for liquid crystalline (LC) substances [2–4]. The $\gamma(T)$-curve deviates in certain temperature ranges, in particular around the bulk phase transitions, distinctly from the normal behavior. Sections with positive or relatively small negative slopes or even discontinuities are observed. The temperature gradient of surface tension of a one-component system, $d\gamma/dT$, relates to the surface excess entropy ΔS^s by $\Delta S^s = (-d\gamma/dT)$ [5]. From this relationship it has to be concluded that sections with positive slopes in a $\gamma(T)$-curve exhibit molecules having higher order at the surface than in the bulk-phase. Surface-induced ordering has therefore to be assumed.

Molecular ordering in the surface zone is more likely to occur for the LC-substances due to the asymmetric (orienting) field conditions, which induce a strong anisotropic potential at the surface, and their strong anisotropic characters. Moreover, such phenomena should especially appear (or be more probably to be observed) at the temperatures near the bulk phase transitions, which may strongly affect the behavior of molecules at the free surface and consequently on the characteristics of surface tension–temperature dependence. Due to the liquid character of the LC mesophases, the surface tension–temperature relationship across the bulk phase transitions is in certain cases experimentally accessible. This provides a novel experimental possibility to explore the behavior of the surface molecules near the bulk phase transitions, which is of interest from both the theoretical and practical point of view, for example in testing the validity of structural models derived from statistical thermodynamics [2, 3].

In a previous study, Song and Springer [3] have observed for some of the studied LC-substances a strong, sharp decrease of the surface tension as the temperature decreases and approaches their crystallization points. The phenomenon was explained by proposing the occurrence of something like surface-induced freezing at the liquid surface. It has been further suggested that such unusual phenomena should be more likely to be observed by those LC substances, which undergo either a transition from the isotropic phase direct into a highly ordered (or crystalline) smectic phase or have a low-temperature highly ordered phase, *e.g.*, highly ordered (or crystalline) smectic or crystalline phase, which exists not far away from the phase transition isotropic → mesophase.

In this paper we report a further investigation for a mesogenic compound *i.e.*, on a member of 4,4′-di-*n*-alkanoyloxybiphenyls which exhibit either a low temperature crystalline or a low temperature highly ordered (crystalline or hexagonal) smectic phase [6]. The results for one compound of the series are reported here. A more detailed investigation will follow and supports the ideas on surface tension stated above.

EXPERIMENTAL

The compound 4,4′-di-*n*-undecanoyloxybiphenyl abbreviated BP-11 (*cf.* Fig. 1 for its chemical structure) was synthesized and purified through recrystallization [6]. The phase behavior was studied by DSC, and the phases identified by texture observation and X-ray measurements. The results are listed in Table I. The compound shows a highly-ordered smectic phase below its clearing temperature [6] and therefore is quite suitable for studying the pretransitional surface induced ordering.

The surface tension as a function of temperature was determined with a computer-aided pendant-drop method [7, 8] and is depicted in Figure 2. Details about the experimental set-up and procedures for the determination of the temperature dependence of interfacial tension of liquid/fluids-systems using this method have been provided in Ref. [3]. The measurement was carried out under N_2 atmosphere. The necessary temperature dependent density $\rho(T)$ of the liquid phase was obtained with an automated precise capillary mercury dilatometer connected to a PC for data acquisition [3, 9]. The density of the gas phase (N_2, 1 atm) was neglected in the calculation. The $\rho(T)$-curve of BP-11 is presented in Figure 3.

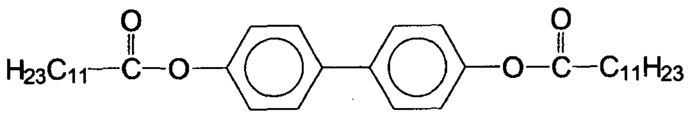

FIGURE 1 Chemical structure of BP-11 (4,4′-di-*n*-undecanoyloxybiphenyl).

TABLE I Phase behavior of BP-11 (DSC-results) [6]

Phase[1]	k_2	k_1	S_G	i
Transition temperature T(°C)	90.9	101.3	122.8	
Transition enthalpy ΔH/(kJ/mol)		26.27[3]	26.81	
Transition entropy $(\Delta S)R^{-1}$ [2]		8.44[3]	8.14	

[1] k_2, k_1, S_G and i denote crystalline 2, crystalline 1, smectic G and isotropic phase, respectively. It is not to exclude that the phase represented here by k_1 may be of nature a highly-ordered liquid crystalline smectic phase.

[2] R is the general gas constant.

[3] The values indicate the total changes in enthalpy and entropy of the phase transitions k_2-k_1 and k_1-S_G.

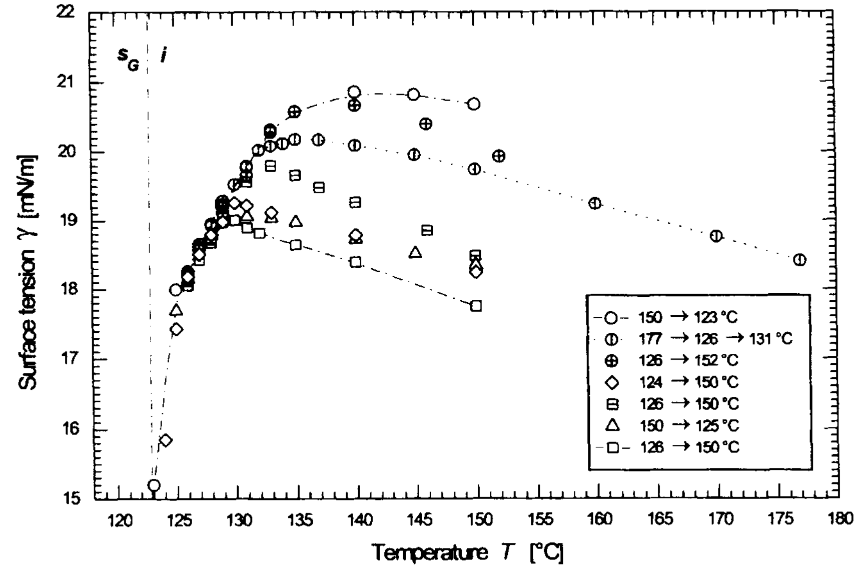

FIGURE 2 Temperature-dependence of surface tension ($\gamma(T)$-curve) of BP-11.

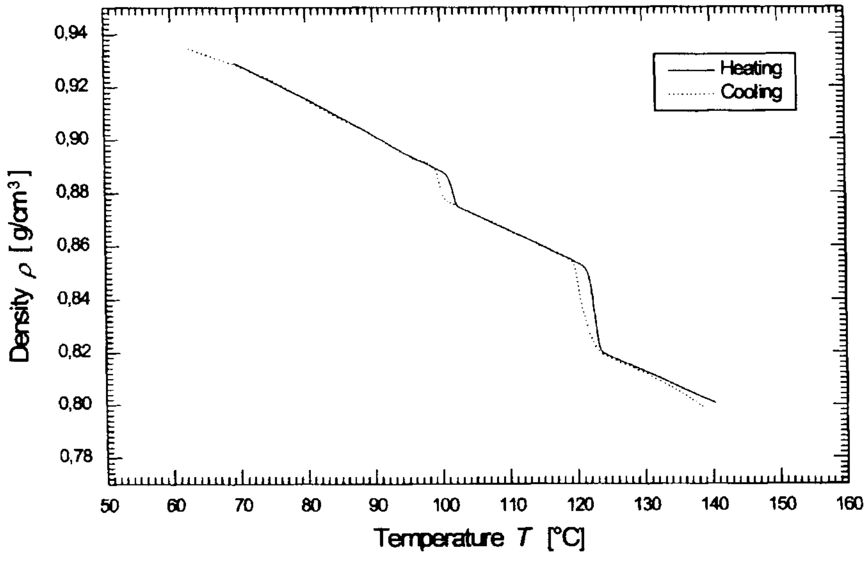

FIGURE 3 Temperature-dependence of density ($\rho(T)$-curve) of BP-11.

RESULTS AND DISCUSSION

As to be seen from Figure 3, the density changes abruptly and to a large extent at the clearing temperature suggesting a transition to a highly ordered phase. For the calculation of the $\gamma(T)$-curve at the high temperature range, of which the $\rho(T)$-curve was not available, the density of the sample was deduced by extrapolation of the $\rho(T)$-curve in the isotropic range.

The $\gamma(T)$-curves as shown in Figure 2 were obtained from a series of measurements, each time using a newly formed liquid drop of which the surface tension was determined either by heating or cooling the liquid drop in steps. In the lower temperature range, the measurements could be carried close to the isotropic → smectic phase transition point. Below this point, the method employed here cannot be used anymore, since the sample was changed to a state which resembles more a solid than a liquid. The drops then formed show profiles which can no longer be described by the Laplace–Young's equation, the basis of the method used [7].

Figure 2 shows that well above the clearing temperature the surface tension of the sample behaves normally, *i.e.*, it increases with decreasing temperature. However, on cooling, the $\gamma(T)$-curve deviates from this normal behavior and becomes anomalous below a certain "inversion" temperature (T_i), that is, it decreases strongly with falling temperature, in particular by approaching the underlying bulk phase transition point.

Well above T_i, the temperature gradient of the surface tension shows a value of about -0.06 ± 0.01 mN/(m·K) and thus lies within the range for the conventional liquids, whereas just below T_i, this value amounts to ca. $+0.3$ mN/(m·K) and increases to ca. $+1.3$ mN/(m·K) near the bulk phase transition temperature. Since the temperature gradient of the surface tension represents for a one-component system the negative surface excess entropy, it can be concluded that above T_i the molecules on the surface are less ordered than in the volume phase and below T_i the opposite is true. At the inversion temperature a change of entropy occurs signifying a phase transition. A further phase transition may be concluded near the clearing temperature of the bulk materials where the slope of the curve changes its value again. Since the measurements in this region are difficult to conduct a clear interpretation cannot be provided. A discontinuous change in entropy suggests a first order phase transition, and a continuous change in entropy a second (or higher) order phase transition. From the $\gamma(T)$-curves shown in Figure 2 it seems that the phase transition at the liquid surface at T_i may be of either first or second order in nature, depending on the experimental conditions.

Figure 2 shows that the inversion temperature changes for different $\gamma(T)$-curves obtained, which leads to deviations in the course of the surface tension – temperature dependence and hence to a remarkable divergence in the absolute values of the surface tension in the high temperature range. Many factors may be involved in the process which causes this divergence. Among them the effects of impurities which could be accumulated (*e.g.*, due to the decomposition of the material) at the liquid surface during the measurement, play probably an important role, since it was observed that the uppermost $\gamma(T)$-curves were more readily to be obtained at the begin of the measurement, whereas those with lower T_i-values were more often encountered at the later phase of the measurement. The accumulation of surface active impurities at the liquid surface will not only reduce the value of the surface tension, but also affects the process and the resulting structure (*e.g.*, domain size) of the possible ordering of the molecules at the surface, and thus the obtained $\gamma(T)$-course as well as the value of the associated "inversion" temperature. The structure and/or ordering of surface molecules are known to be rather sensitive to the presence of other molecular species [2].

The different heating or cooling programs used to obtain the different $\gamma(T)$-curves, mainly the different heating or cooling rates involved, may also be considered as a factor which could principally affect the $\gamma(T)$-course and the T_i-value, too. But its role should be small if not negligible.

It is interesting to compare the behavior of the surface tension – temperature dependence of the here examined BP-11 exhibiting long alkyl end groups with that of the normal alkanes. Earnshaw and Hughes [4] have studied the temperature-dependence of surface tension of several n-alkanes with n between 15 and 18 using the Wilhelmy plate method. They found for these substances a quite similar $\gamma(T)$-behavior as that observed for BP-11: the $\gamma(T)$-curves of these substances were observed to change to a monotonic decrease by reducing the temperature below a certain, substance dependent value close to the freezing point. This value lies about 2 K and 1 K above the melting point for n-heptadecane and n-octadecane, respectively. The positive $d\gamma/dT$-value below the inversion point varies with the chain length of n-alkanes and increases nearly linearly from about $+0.33\,\mathrm{mN/(m\cdot K)}$ for n-pentadecane to ca. $+0.91\,\mathrm{mN/(m\cdot K)}$ for n-octadecane. The later value is quite comparable to that of BP-11 with ca. $+1.3\,\mathrm{mN/(m\cdot K)}$ for the temperature range in close vicinity to the bulk phase transition point.

From the aspect of the arrangements of the molecules, there exist some similarities between BP-11 and n-alkanes, since the packing of BP-11 is dominated through its aliphatic part, particularly insofar as its surface properties are considered. Both compounds exhibit a similar triclinic subcell for a C_2H_4 group [6]. However, due to the liquid crystalline underlying bulk phase of BP-11, the effect of the surface induced ordering occurs more distinctly at the surface of BP-11 than on a comparable *n*-alkane. While the anomaly in the $\gamma(T)$-curves appears for the *n*-alkanes only by reducing the temperature very closely to (or even below) their freezing points, it can be observed for BP-11 clearly by temperatures more than 10 K above the underlying phase transition point.

The results of this study reveal that, as suggested in a previous paper [3], the existence of a nearby low-temperature highly-ordered phase (either a crystalline or a highly ordered smectic phase) seems to favor the formation of a highly ordered molecular layer at the free surface. Recent ellipsometric and X-ray reflectivity measurements support the molecular order at the liquid interface and indicate that highly ordered or "smectic-like" layer structures [10–15] may exist in the surface layer and maintain even in a temperature range well above their clearing points [15]. Such phenomena should particularly be observed for those LC substances which possess low-temperature highly ordered phases [10, 11, 15].

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References

[1] R. Eötvös, *Wied Ann.*, **27**, 448 (1886).
[2] B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **293**, 39 (1997), and the references cited therein.
[3] B. Song and J. Springer, *Mol. Cryst. Liq. Cryst.*, **307**, 69 (1997).
[4] J. C. Earnshaw and C. J. Hughes, *Phys. Rev. A*, **46**, R4494 (1992).
[5] L. Dufour and R. Defay, *Thermodynamics of Clouds*, Academic Press, New York and London (1963), Chapter 3.
[6] W. Thyen, *Doctoral-thesis*, Technical University of Clausthal (1995).
[7] B. Song and J. Springer, *J. Colloid Interface Sci.*, **184**, 64 (1996).
[8] B. Song and J. Springer, *J. Colloid Interface Sci.*, **184**, 77 (1996).
[9] T. Runke, *Doctoral-thesis*, Technical University of Berlin (D83), (1994).
[10] B. M. Ocko, A. Braslau, P. S. Pershan, J. Als-Nielsen and M. Deutsch, *Phys. Rev.-Lett.*, **57**, 94 (1986).
[11] P. S. Pershan, A. Braslau, A. H. Weiss and J. Als-Nielsen, *Phys. Rev.*, **A35**, 4800 (1986).
[12] D. Beaglehole, *Mol. Cryst. Liq. Cryst.*, **89**, 319 (1982).

[13] J. W. Done, A. Golemme, J. L. West, J. B. Whitebread, Jr. and B.-G. Wu, *Mol. Cryst. Liq. Cryst.*, **165**, 511 (1988).
[14] S. Immerschitt, T. Koch, W. Stille and G. Strobl, *J. Chem. Phys.*, **96**, 6249 (1992).
[15] H. Elben and G. Strobl, *Macromolecules*, **26**, 1013 (1993).