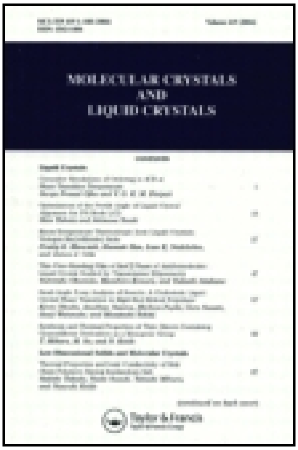

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P-T Diagrams of Phase State of Nematic Liquid Crystals

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P-T DIAGRAMS OF PHASE STATE OF NEMATIC LIQUID CRYSTALS

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Abstract P-T diagrams of phase state of MBBA, EBBA, 6OCB and p-hexyloxiphenyl-p'-butylbenzoate (H-21) are built on the base of tensimetric data. Heats of phase transitions and changes in evaporation enthalpies are calculated.

INTRODUCTION

Progress of science and technology put forward the task of creation of materials with definite properties. First of all this concerned the means of obtaining new materials when synthesis was performed in deep vacuum. Hence, gaseous phase acquired greater role in high-temperature technology, since saturated vapour pressures became comparable with external pressure. It became necessary to consider pressure as a variable possessing equal rights and to come back to the studies on P-T and T-x diagrams of phase state. However, experimental works carrying P-T-, T-x- and P-x-projections are few. This is connected with the fact that determination of the saturated pressure comes across considerable difficulties.

EXPERIMENTAL

Measurements of the saturated vapour pressure were performed by the static method on a tensimetric plant with quartz nil-manometer of spoon type. The plant and experimental technique is described in detail in the previous works[1,2]. All the liquid crystals used were of "RIAP", USSR origine; they were additionally refined by sublimation in vacuum.

DISCUSSION

Diagrams within P-T coordinates should be considered the most convenient form for a full description of the phase equilibria in closed systems.[3] Description of the states of mono-componential system within these coordinates allows one to use the intensive parameters, i.e. does not require consideration and account of mass of substance. Two-phase states in such a diagram are represented clearly enough by simple lines the analytical imprints of which are theoretically substantiated. Features of these diagrams ensured first of all direct determination of the values of the most important parameters of state P, T and made possible calculations of thermodynamic parameters of the phase transformations ΔH and ΔS.

Figure 1 shows the phase diagrams of MBBA, EBBA, H-21 and 6OCB built on the base of the tensimetric data that were obtained before.

A slight change in volume is a peculiarity of the phase transitions in the systems with condensed phases. For many cases of melting of individual substances the melting curve can be represented in a form of a straight line which differs slightly from a vertical line. At the melting point T_m the heat capacity of a solid changes little with temperature.[4] The heat capacity of melted substance is also so dependent on temperature, that one can assume near T_m the ratio

$$\frac{\Delta H_m}{T_m} = \Delta S_m$$

is independent of pressure and temperature and,

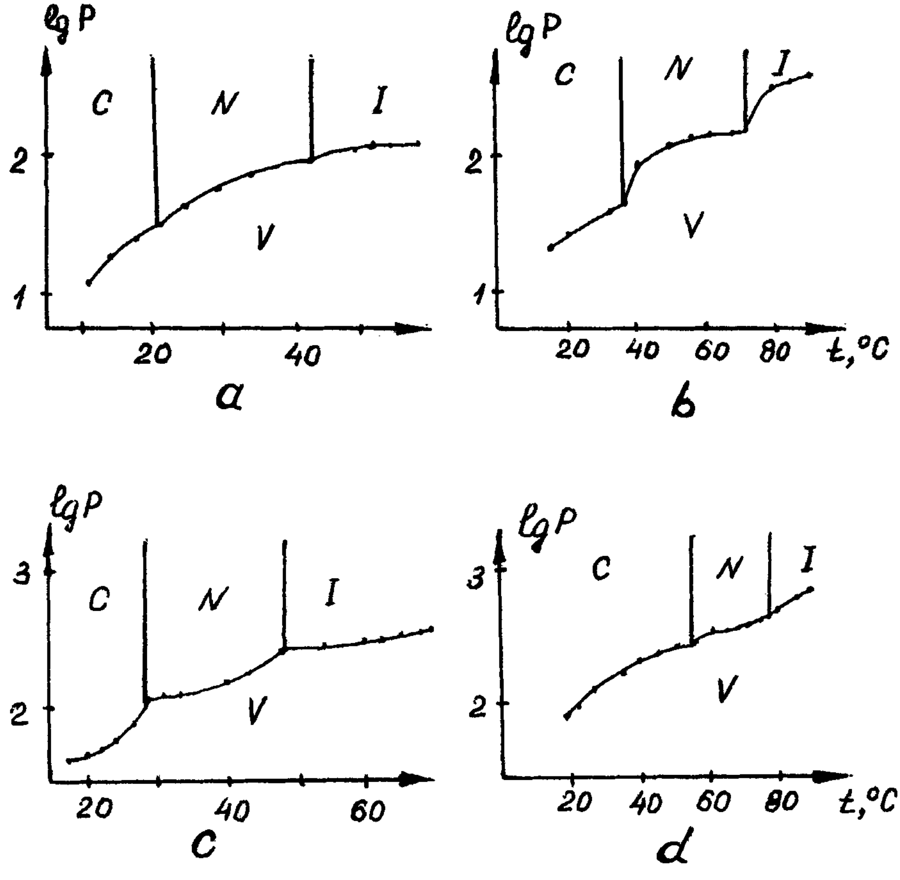

FIGURE 1. Phase diagrams: a)MBBA; b)EBBA; c)H-21; d)6OCB.

consequently, the line of the phase border crystal-melt will be straight.

It is noteworthy that all the processes depicted in the diagrams of state assume reversibility and movement through a continuous set of consecutive equilibrium states, which in its turn is determined by the possibility of a simultaneous equilibrium of all the phases in a system.

Individual substances are known to be able to form only one vapour phase, several liquid and several solid phases. The rule of phases allows to characterize the phaseous composition of mono-component systems. Regions C, L (N, I), V correspond to non-variant equilibrium of a system.

The states given as lines in the diagrams correspond to monovariant two-phaseous equilibria: C-V; N-V; I-V; C-N; N-I.

Results of tensimetric investigations expressed in the form of Clausius-Clapeyron equation served as the basis for calculation of the change in enthalpy of transition condensed phase-vapour. Table I presents the values of sublimation and evaporation enthalpies and

TABLE I Change in evaporation enthalpy and phase transition enthalpy (kJ/mole) of liquid crystals

Liquid crystals	ΔH_V^C	ΔH_V^N	ΔH_V^I	ΔH_{C-N}	ΔH_{N-I}
MBBA	35.97	13.61	9.907	22.35	3.70
EBBA	30.05	7.12	2.58	22.92	4.53
H-21	78.64	31.04	22.25	47.59	8.79
60CB	24.83	20.35	-	4.47	-

enthalpies of nematic liquid crystals.

Calculated magnitudes of the change in enthalpy of phase transitions yield satisfactory coincidence with experimental data (of +10% order) obtained by calorimetric method.[5,6]

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