Plotting of phase (vapor-liquid) transition surface near the critical point out of data from isochoric experiment. Experimental procedure

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ABSTRACT

This paper suggests a mathematical model of processing experimental data that allows to plot the surface of the phase transition in near critical region, using the results of isochoric experiment. The model is based on proven approximation methods. The model was tested on 20 binary mixtures (10 mixtures of C_2-C_7 linear alkanes, five mixtures of propane and branched C_5-C_6 alkanes, two mixtures of haloalkanes, one mixture each of pentane with toluene, cyclohexane with benzene and toluene) with the difference in critical temperatures from 45 to 235 K. As the result, in the $0.5 \leq \rho_{Dew}/\rho_c < 1.5$ range of reduced density the average error in predicting temperatures of phase transition is 2.2 K, 1.2 K for critical temperatures, 3 K for maximum temperature of liquid and vapor phase coexistence.

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1. Introduction

Processes based on critical state of matter are now being actively developed [1—4]. Information on critical properties of the reaction mixture components is essential for development of such technologies. Apart from studying critical temperatures ($T_{c,m}$), it is also important to obtain new data on maximum temperatures of liquid and vapor phase coexistence (maximum temperature or $T_{max,m}$). This is especially essential for the production of mesoporous materials, for example, aerogels.

Obtaining this information is a very labor intensive and time consuming process, especially if the components differ greatly in their critical properties. The reason is that the complete phase diagram for each composition has to be determined experimentally, due to the critical point location is unique for each mixture [5,6]. Ignoring this stage of experiment may lead to significant deviation between the experimentally obtained temperature ($T_{Dew,m}$) and the actual critical point [6].

The reason why the deviations occur is the change in the phase diagram in the "temperature-density" dimensions with increasing difference between critical temperatures of the mixture components ($\Delta T_{c(i,j)}$).

The greater the value of $\Delta T_{c(i,j)}$, the more rapid is the change of the function $T_{Dew,m} = f(\rho_{Dew,m})$ (Fig. 1), and, therefore, a smaller difference in density is resulted in more significant change in temperature. The analysis of literary data leads one to the conclusion that this trend is observable regardless of the class of the substances that compose the mixture. It is observed both for alkane mixtures (Fig. 1), and for the mixtures of alkanes and aromatic hydrocarbons and for mixtures of haloalkanes (Fig. 1).

Therefore, the acquisition of technically valuable data is taking more time than the rapid pace of supercritical technologies development demands. A possible solution to this problem is to develop a new approach to obtaining and description of experimental data that would allow constructing a phase transition surface ($T_{Dew} = f(\text{density, composition})$) out of a limited data set. Such approach will make it possible to obtain not only reliable information on critical properties of mixtures, but also data on their phase equilibrium near the critical point, regardless of composition.

The main idea that lies in the foundation of the new procedure of experiment and experimental data processing is to make it unnecessary to rely on empirical data of the critical properties at fixed mixture composition (as in Refs. [6—17]). This significantly decreases the amount of experimental work due to simultaneous use of the dependence of phase change temperature on density and composition of the mixture for processing of the experimental data.

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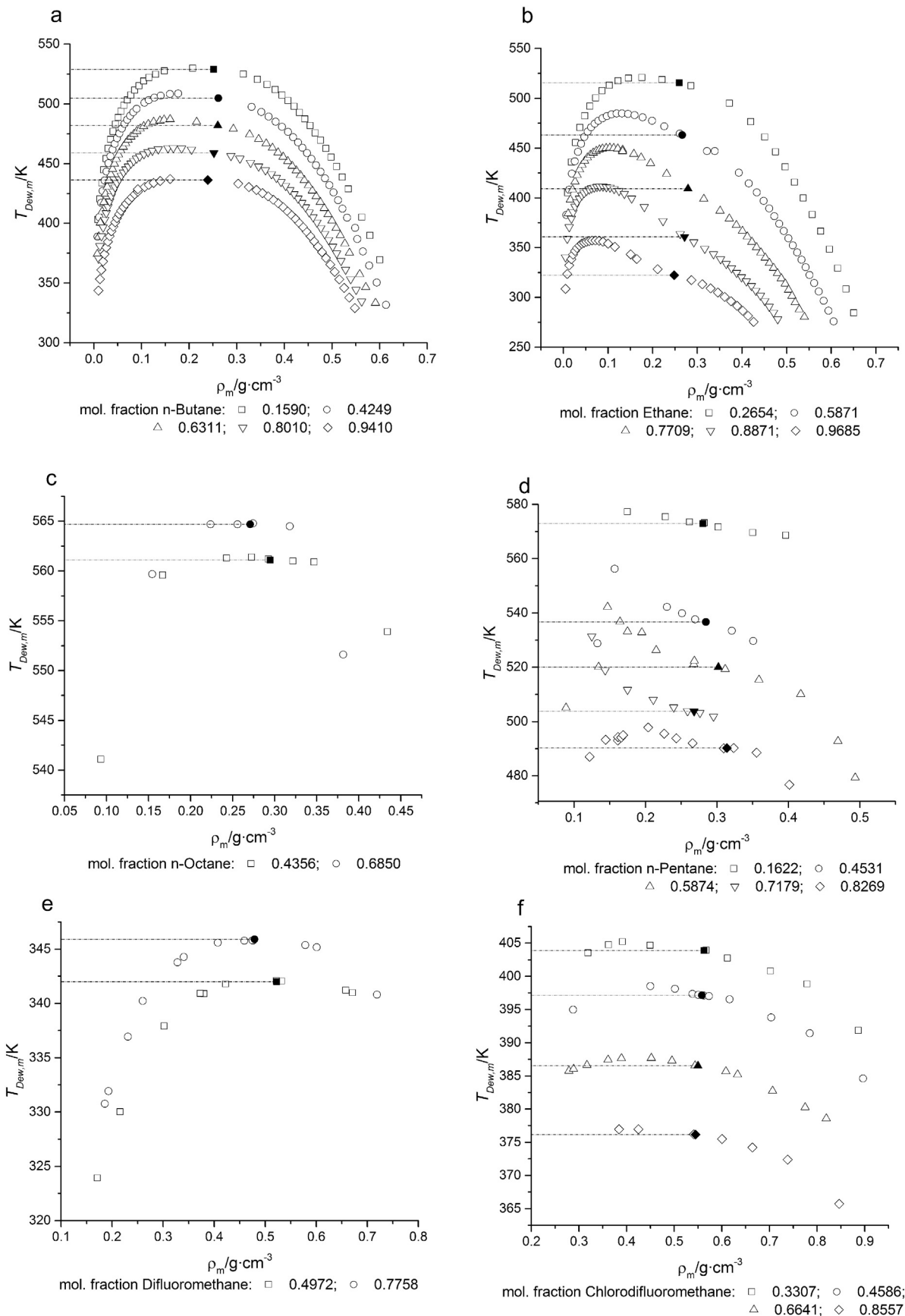
Fig. 1. Phase diagrams (temperature-density) of binary mixtures.
a − n-Butane + n-Heptane [13] ($\Delta T_{c(i,j)}$ = 115.1 K); b − Ethane + n-Heptane [8] ($\Delta T_{c(i,j)}$ = 234.9 K); c − n-Octane + Benzene [6] ($\Delta T_{c(i,j)}$ = -7.3 K); d − n-Pentane + Toluene [6] ($\Delta T_{c(i,j)}$ = 122.1 K); e − Difluoromethane + Pentafluoroethane [17] ($\Delta T_{c(i,j)}$ = −12.1 K); f − Chlorodifluoromethane+1,2-Dichlorotetrafluoroethane [16] ($\Delta T_{c(i,j)}$ = 49.5 K); Black points − critical temperatures.