ANALYSIS OF DIMERIZATION EQUILIBRIUM DEVIATIONS FROM IDEALITY IN MIXTURES WITH INTERACTION IN THE FORM OF THE SQUARE WELL

Davydov A.G., * *Tkachev N.K.*

IHTE UB RAS, Ekaterinburg, Russia
*A.Davydov@ihte.uran.ru

The analysis of chemical equilibrium in nonideal associated liquids is a sufficiently complex problem in statistical thermodynamics, since the interaction of associates and monomers in a dense liquid must lead to a certain shift in chemical equilibrium. The result depends on the nature of the intermolecular forces acting between the particles in the mixture.

The purpose of the present work was to analyze the influence of short-range attraction on the deviations of chemical equilibrium from ideality in a liquid mixture of monomers and dimers.

The attraction in the dimerizing mixture is accounted for by the pair potential of the square well. Moreover, the spontaneous dimerization reaction proceeds together a change in volume, depending on the degree of fusion of the monomers in the dimer.

To determine the equilibrium position of such liquid mixture, it is necessary to find the minimum of the Gibbs free energy with respect to two independent variables: the volume and dimer concentration. Moreover, it is reasonable to use the mean activity coefficient (in the equation of the mass action law), namely, in which (not in the equilibrium constant) all intermolecular interactions should be taken into account.

As a result, it was shown that an increase in attraction between monomers leads to a shift in equilibrium towards dissociation, while an increase in attraction between dimers plays an inverse role. Accounting attraction leads to an increase in the packing fraction, particularly in the case of greater attraction between dimers and smaller bond lengths. Under these conditions, the maximum tendency to ordering the liquid is observed.