SEMIEMPIRICAL KIRKWOOD-BUFF INTERPRETATION FOR ISOTHERMAL COMPRESSIBILITY EXCESS OF LIQUID BINARY MIXTURES

O. I. Gerasymov, F. Aliotta+ and C. Vasi+

Odessa State Environmental University, Odessa, Ukraine
+Consiglio Nazionale delle Ricerche (CNR), Istituto per i Processi Chimico-Fisici, Messina, Italy
gerasymovoleg@gmail.com

Kirwood-Buff approach has been applied to describe the isothermal compressibility excess of binary mixtures in terms of parameters of the reference systems by means of superposition of theoretical constructions and phenomenological data.
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In describing any structuring effect resulting from mixing in any multicomponent system, the relevant information can be get from the knowledge of the values of the thermodynamic parameters as volume, pressure, temperature and chemical potential. In principle, one can be led to imagine that a comparison of the state functions of the mixture with those corresponding to the pure components can be enough for extracting information about the nature of the interaction among components. Even if such an approach is widely adopted, it should be clear that it faces us immediately with the difficulty of introducing a number of definitions and approximations.

A relatively simple example can be represented by the binary mixture of two pure liquids which are able to dissolve one into the other over the whole range of possible concentrations. If one would be able to define a reference system, in which the two pure components have exactly the same properties of the real systems and in which the properties of the mixture are not affected by the mixing, then the play would be done. Any deviation of the properties of the real system from those of the reference system can be immediately assigned to the interaction between the components after the mixing. Following such an approach the reference systems is immediately individuated: it should be a system where i) each of the two components has no tendency towards self-aggregation; ii) the two existing species have no tendency to aggregate one each the other; iii) no structuring effect takes place due to excluded volume interactions. Strictly speaking, the condition i) and ii) can be related with the chemical nature of the two species but the condition iii) implies the assumption of a vanishing density. Apparently we have reached the conclusion that a low

density mixture of the two components, i.e. a gas-like system, can represent a good candidate as the reference system. Once the reference has been individuated, we have just to compare the experimental values with the prevision from an ideal model following the Raoult's law. It is quite obvious how the above defined reference state can be over-simplified. In dealing with systems characterized by a not negligible density any comparison with ideal behaviors must be taken with serious caution. Ideality implies the assumption that each of the volumetric and energetic properties of the mixture can be written as the linear combination of those of pure components, weighted by their relative concentrations. The idea arises from the observation that any quantity can be locally expressed as a linear expansion, which means that can be locally approximated by the tangent at its representative curve in the point of interest. But the extrapolation of the linear behavior towards the pure component often shows the existence of some divergence, which means that the pure component alone can be affected by excess volume. One can try to overcome such a difficulty reversing the perspective, i.e. adopting the experimental value for one of the pure components as the reference and linearly extrapolating this value making it vanishing. The present paper is devoted to semiempirical interpretation of the excess properties of simple binary mixtures with help of Kirkwood-Buff theory (KB) which formally based on determination of statistical correllational integrals [1]. We propose semiempirical Pade-interpolation of KB expression which we made selfconsistent after superimosition with experimental information concerarned isothermal compressibility of selected binary mixtures. By use of this semiempirical construction we got an output in form of expression for isothermal compressibility excess which depends only from the concentrations of the components and the partial parameters of the reference systems. Theoretical description described upper, we compare with experimental study of / binary mixture .We got satisfactory agreement of theoretical results and experimental data (which has been extracted from the sound speed measuring [2]).

References

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