【別紙２】

論文名：Dynamic Behavior of Mesoscopic Concentration Fluctuations in Aqueous Solutions of 1-Propanol by MD Simulation（要約）

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Concentration fluctuation is one the main interests in the physical chemistry of liquid mixtures, snice it is a measure of local immiscibility in the mixtures. In this study, we explore the possibility of molecular simulation in evaluating concentration fluctuation quantitatively and comprehensively. The comprehensive evaluation here means the direct calculation of concentration fluctuation using our original method [1], the evaluation of the Kirkwood-Buff integrals from the radial distribution functions, and furthermore mutual conversions between concentration fluctuation and the Kirkwood-Buff integrals using the conversion relations by Nishikawa [2]. In order to validate such an idea of the comprehensive estimation of concentration fluctuations, we first applied the present method to simple liquid mixtures of Ar and Kr. In order to improve estimations quantitatively, molecular number included in the system was increased up to more than 10,000. As a more interesting system having significant amplitude of concentration fluctuation, we performed MD simulations of aqueous solutions of 1-propanol, and evaluated both concentration fluctuations and the Kirkwood-Buff integrals. In the present study, we also focus on the time variation of these quantities which have never been discussed in the literatures.

In Chapter 1, we describe both the history and the present status of studies of concentration fluctuations in liquid mixtures, in addition to the above-stated significance and purpose of the present study. In Chapter 2, we explain the calculation method commonly used in the present work. In Chapter 3, we describe the results of MD simulations of liquid mixtures of Ar and Kr, and the results of evaluation of the concentration fluctuations using direct counting method and the Kirkwood-Buff integrals from the pair correlation functions. Furthermore, using the mutual conversion relations between the concentration fluctuations and the Kirkwood-Buff integrals, we discussed the Kirkwood-Buff integrals obtained from the concentration fluctuations and *vice versa*. As a result, we found that both the evaluation results of concentration fluctuations from direct counting method and from the Kirkwood-Buff integrals based on the pair correlation functions are in good agreement with each other. Furthermore, we found that both the evaluation results of the Kirkwood-Buff integrals from the concentration fluctuations and from the pair correlation functions are also in good

agreement with each other, and also with the experimental results. Thus, we conclude that the present direct counting method is useful not only for evaluating the concentration fluctuations but also for evaluating the Kirkwood-Buff integrals in the simple liquid mixture. In Chapter 4, we describe the results of MD simulations of aqueous solutions of 1-propanol with molar fraction of 1-propanol $x_P = 0.1$ and 02, and the results of the evaluation of the concentration fluctuations using the direct counting method and the Kirkwood-Buff integrals from the pair correlation functions. We found the time variation in both the amplitude of concentration fluctuations and the Kirkwood-Buff integrals in nanosecond time scale: This is a novel finding in the simulation works regarding this topic. Furthermore, also in these solutions, using the mutual conversion relations between the concentration fluctuations and the Kirkwood-Buff integrals, we obtained the Kirkwood-Buff integrals from the concentration fluctuations and *vice versa*. As a result, we found that both the evaluation results of concentration fluctuations from the direct counting method and from the Kirkwood-Buff integrals based on the pair correlation functions are in good agreement with each other. Furthermore, we found that both the evaluation results of the Kirkwood-Buff integrals from the concentration fluctuations and from the pair correlation functions are also in good agreement with each other, and also with the experimental results. Thus, also in the solutions, we conclude that the present direct counting method is useful not only for evaluating the concentration fluctuations but also for evaluating the Kirkwood-Buff integrals.

As one of the advantages of the present method, we have successfully demonstrated that the present method can provide quantitative information of spatial distribution of concentration fluctuation which upgrades qualitative information such as the conventional snapshot of molecular configuration. By combining the above-stated finding that the fluctuations are time-dependent in the nanosecond scale, we also have successfully demonstrated the time variation of spatial distribution of concentration fluctuation. This enables us to access the quantitatively visualized information of the dynamic behavior of the mesoscopic concentration fluctuation in liquid mixtures.

[1] M. Ogawa, Master thesis, Graduate School of Science and Technology, Niigata University, (2002).

[2] K. Nishikawa, *Chem. Phys. Lett.*, 132, 50(1986).