Estimation of Parameters, G_{11}, G_{22}, and G_{12} in the Kirkwood-Buff Solution Theory on the Basis of the Concentration Fluctuation Data Obtained from Rayleigh Scattering

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A concentration fluctuation value obtained from Rayleigh scattering intensity was confirmed to give a thermodynamic quantity of an equilibrium system. An observation of concentration fluctuation by a light scattering method was found to be the most direct and useful way of determining a concentration derivative of a chemical potential. For methanol, ethanol, and 1-propanol–carbon tetrachloride systems, the Kirkwood-Buff parameters, G_{11}, G_{22}, and G_{12}, were determined by the use of concentration fluctuation data. The structure of these systems was discussed on the basis of the calculated Kirkwood-Buff parameters.

The solution theory of Kirkwood and Buff is only one theory so far reported which can describe a thermodynamic properties of a solution for the whole concentration range.[1–4] This theory relates thermodynamic quantities of a system to the radial distribution function $g(r)$ through a "concentration fluctuation." In this theory, a parameter G_{ij} plays an important role, which is defined as,

$$G_{ij} = \int_0^\infty \{g_{ij}(r) - 1\} 4r^2 dr, \tag{1}$$

where $g_{ij}(r)$ is the radial distribution function between species i and j. It is important to notice that $g_{ij}(r)$ is a microscopic expression of the structure of a solution. In the case of a binary solution, the parameters G_{11}, G_{22}, and G_{12} appear in this theory. As $g_{ij}(r)$ is an observable quantity by an X-ray or a neutron diffraction method, G_{ij} is also an observable by these methods in principle. In practice, however, these measurements can not give separately each value of $g_{ij}(r)$. Therefore, it is of much importance to determine the G_{11}, G_{22}, and G_{12} values experimentally from macroscopic quantities such as molar volume, compressibility, concentration dependences of chemical potential, and other thermodynamic quantities. Because of the difficulty of obtaining the $(\partial\mu_2/\partial x_2)_{P,T}$ value experimentally with high accuracy, however, such attempts have been reported in only a few papers.

Ben-Naim estimated the concentration dependence of G_{ij} in binary solutions of ethanol and water based on the concentration dependence of the vapor pressure.[5] Similarly, Donkersloot[6] has determined G_{ij}'s for binary solutions of cyclohexane–2,3-dimethylbutane, methanol–water, and ethanol–water. He also calculated the zero-angle X-ray scattering intensities from the G_{ij} values so obtained and compared them with the experimental data.[6,7]

Kato and Fujiyama have discussed the local structures in various solutions on the basis of the quantitative analysis of the concentration fluctuation, $V^*\langle(\Delta x_2)^2\rangle$, obtained from the Rayleigh scattering intensities[8–14] where V^* refers to the volume of the region in which concentration fluctuation is considered. If V^* is large enough to permit the application of statistical mechanics, $V^*\langle(\Delta x_2)^2\rangle$ can be directly related to the concentration derivative of the chemical potential.

In the present work, we will evaluate the Kirkwood-Buff parameters G_{11}, G_{22}, and G_{12}, for binary solutions of methanol–carbon tetrachloride, ethanol–carbon tetrachloride, and 1-propanol–carbon tetrachloride by the use of the concentration fluctuation data obtained from the Rayleigh scattering intensity measurement.[14] We will emphasize the usefulness and reliability of the concentration fluctuation data obtained from the light scattering experiment. At the same time, the structure of the carbon tetrachloride–alcohol systems will be discussed on the basis of the calculated Kirkwood-Buff parameters.

Concentration Fluctuation Obtained from Rayleigh Scattering Intensity and Thermodynamic Property

We first examine the concentration fluctuation values obtained from a light scattering experiment. The concentration fluctuation of a solution can be expressed in terms of the excess chemical potential μ_2^{E} [14] or of the excess free energy G^E as

$$N\langle(\Delta x_2)^2\rangle = \frac{x_1 x_2}{1 + \frac{x_2}{RT}\left(\frac{\partial \mu_2^{E}}{\partial x_2}\right)_{P,T}} \tag{2}$$

or

$$N\langle(\Delta x_2)^2\rangle = \frac{x_1 x_2}{1 + \frac{x_1 x_2}{RT}\left(\frac{\partial^2 G^E}{\partial x_2^2}\right)_{P,T}} \tag{3}$$

$$G^E = x_1\mu_1^{E} + x_2\mu_2^{E}, \tag{4}$$

where x_1 and x_2 are the mole fractions of 1 and 2, respectively, μ_1^{E} and μ_2^{E}, the excess chemical potentials of 1 and 2, respectively, R the gas constant, P the pressure, and T the temperature. N of the left of Eq. 1 or 2 is the total number of molecules in the volume V^* ($N=\rho V^*$, ρ: the number density of the solution). Equation 2 enables us to calculate the $(\partial\mu_2^{E}/\partial x_2)_{P,T}$ values using the $N\langle(\Delta x_2)^2\rangle$ values obtained from the light scattering experiment[14] and compare them with those obtained from the vapor-liquid equilibrium experiments.[15] In these calculations, μ_2^{E} was calculated from the vapor pressure data, and was plotted against the concentration. The $(\partial\mu_2/\partial x_2)_{P,T}$ value was derived graphically. The Gibbs-Duhem relation, $x_1(\partial\mu_1/\partial x_2) + x_2(\partial\mu_2/\partial x_2) = 0$, was carefully taken

into account in this process. The results are illustrated in Fig. 1. As shown in Fig. 1, the $-(\partial\mu_2^E/\partial x_2)_{P,T}$ values obtained from these two different procedures agree with each other satisfactorily within their experimental errors. In other words, V^* is ascertained to be large enough to permit the application of statistical mechanics.

In most reports on solution chemistry, G^E is given by a polynomial formula. For example, the excess Gibbs' free energy for the methanol–carbon tetrachloride is given by two relations, one proposed by Scatchard *et al.*[16] and the other by Moelwyn-Hughes *et al.*[17] These empirical formulae give almost the same G^E values. However, if we calculate the concentration fluctuation values $N\langle(\Delta x_2)^2\rangle$, using these two empirical formulae through Eq. 3, the results are completely different with each other. Of course they don't agree with those obtained from the light scattering data shown in Ref. 14. These situations are illustrated in Fig. 2. The results indicate that the given polynomial formulae of G^E do not well express their second derivative, *e.g.*, $(\partial^2 G^E/\partial x_2^2)_{P,T}$ with sufficient accuracy. In other words, it is not easy to predict the concentration fluctuation values from the observed free energy data, although it is possible in principle. By the same reason, it is also difficult to predict the chemical potential values from the concentration fluctuation values obtained by light scattering experiments.[18]

Thus, we can conclude as follows:

(1) A concentration fluctuation value obtained from Rayleigh scattering intensity is a thermodynamic quantity of an equilibrium system.

(2) An observation of concentration fluctuation by a light scattering method is the most direct and useful way of determining a concentration derivative of a chemical potential.

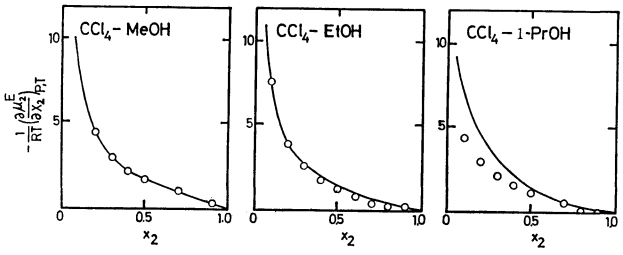

Fig. 1. Plots of $-(1/RT)(\partial\mu_2^E/\partial x_2)_{P,T}$ *vs.* x_2 (suffix 2 refers to alcohol).
○: Calculated from concentration fluctuation data by light scattering, ——: calculated from vapor-liquid equilibrium data.

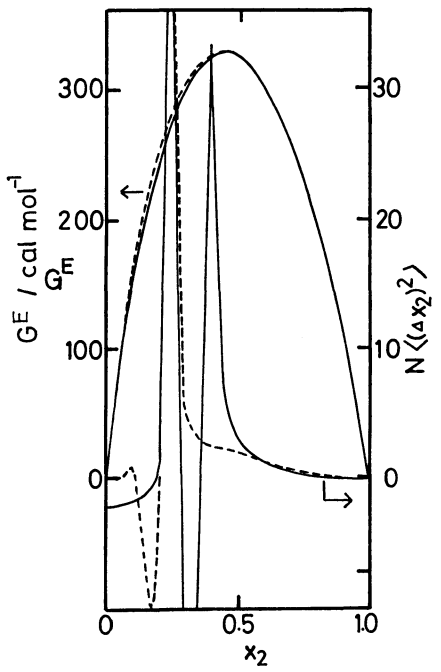

Fig. 2. Excess Gibbs' free energy calculated by empirical formulae proposed by Scatchard *et al.*[16] (——) and Moelwyn-Hughes *et al.*[17] (……) and concentration fluctuation values $N\langle(\Delta x_2)^2\rangle$ calculated from Eq. 3 for carbon tetrachloride–methanol system at 35 °C.

Determination of the Kirkwood-Buff Parameters, G_{11}, G_{22}, and G_{12}, for CCl_4–Methanol, CCl_4–Ethanol, and CCl_4–1-Propanol Systems

According to the Kirkwood-Buff theory, the partial molar volumes v_1, v_2, the isothermal compressibility, κ_T, and the concentration derivative of the chemical potential, $(\partial\mu_2/\partial x_2)_{P,T}$ can be expressed as functions of G_{11}, G_{22}, G_{12}, ρ_1, and ρ_2 where ρ_1 and ρ_2 are the number densities of 1 and 2, respectively. Therefore, G_{11}, G_{22}, and G_{12} can be obtained from these thermodynamic quantities.[5] For numerical calculations, the following data were used.

The concentration derivative of the chemical potential, $(\partial\mu_2/\partial x_2)_{P,T}$ was calculated from the data on the concentration fluctuation obtained from Rayleigh scattering.[14]

Density data for carbon tetrachloride–methanol,[16,19,20] carbon tetrachloride–ethanol,[21] and carbon tetrachloride–1-propanol[20] systems are found in the literature. From these data, the partial molar volumes of each system are calculated.

The isothemal compressibility can be expressed in terms of the adiabatic compressibility, κ_s, the thermal expansion coefficient, α, and the isobaric heat content, C_P, as

$$\kappa_T = \kappa_s + \frac{TV\alpha^2}{C} \qquad \alpha \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P. \tag{5}$$

The isobaric heat content for the solution was calculated from that of the pure component and the temperature dependence of the mixing enthalpy.[22] The expansion coefficent for the carbon tetrachloride–methanol system was calculated from the temperature dependence of the density.[23] For the carbon tetrachloride–ethanol and carbon tetrachloride–1-propanol systems, the data of the temperature dependence of the density can not be found in the literature. So, we evaluated α values from those for the pure alcohol and carbon tetrachloride taking into account the concentration dependence of α for the carbon tetrachloride–methanol system.

The adiabatic compressibility is related to the sound velocity, u_s, by the Laplace equation:

$$\kappa_s = \frac{1}{du_s^2}, \tag{6}$$

where d is the density. The sound velocities for the carbon tetrachloride–ethanol and carbon tetrachloride–1-propanol systems were measured using an ultrasonic interferometer which was operated at a fixed frequency of 5.000 MHz. For the carbon tetrachloride–methanol system, the data of Nomura *et al.*[23] were used.

Discussion

Limiting Values of G_{11}, G_{22}, and G_{12}. Figures 3—5 show the concentration dependences of G_{11}, G_{22}, and G_{12}. For the pure liquids, 1 and 2, G_{11} and G_{22} are expressed as

$$G_{11}^{\circ} = -\frac{1}{\rho_1} + \kappa_{T_1} kT$$

$$G_{22}^{\circ} = -\frac{1}{\rho_2} + \kappa_{T_2} kT.$$

It can be seen from Fig. 3 that the limiting value of G_{11} at $x_2 \to 0$ coincides with G_{11}° value for pure carbon tetrachloride which is $G_{11}^{\circ} = -94.3$ cm^3 mol^{-1}. At the same time, each limiting value of G_{22} at $x_1 \to 0$ coincides with the G_{22}° value for each alcohol ($G_{22}^{\circ} = -37.6$ cm^3 mol^{-1} for methanol, -55.8 cm^3 mol^{-1} for ethanol, and -72.6 cm^3 mol^{-1} for 1-propanol).

The limiting value of G_{12} at $x_1 \to 0$ and $x_2 \to 0$ are expressed as

$$\lim_{x_1 \to 0} G_{12} = \frac{1}{\rho_2} - \bar{v}_1^{\circ} + G_{22}^{\circ}$$

$$= -93.4 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{MeOH-CCl}_4)$$

$$= -92.8 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{EtOH-CCl}_4)$$

$$= -92.8 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{1-PrOH-CCl}_4),$$

$$\lim_{x_2 \to 0} G_{12} = \frac{1}{\rho_1} - \bar{v}_2^{\circ} + G_{11}^{\circ}$$

$$= -38.4 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{MeOH-CCl}_4)$$

$$= -57.0 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{EtOH-CCl}_4)$$

$$= -84.8 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{1-PrOH-CCl}_4),$$

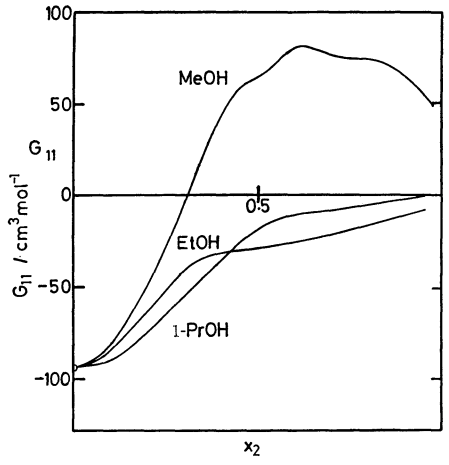

Fig. 3. Concentration dependence of G_{11}.

where $\bar{v}_1^{\circ}$ and $\bar{v}_2^{\circ}$ are the partial molar volumes at infinite dilution. Figure 5 shows that the values of G_{12} tend smoothly to these limiting values. The behavior of these limiting values of G_{11}, G_{22}, and G_{12}, on each side, indicates that the estimation of these value

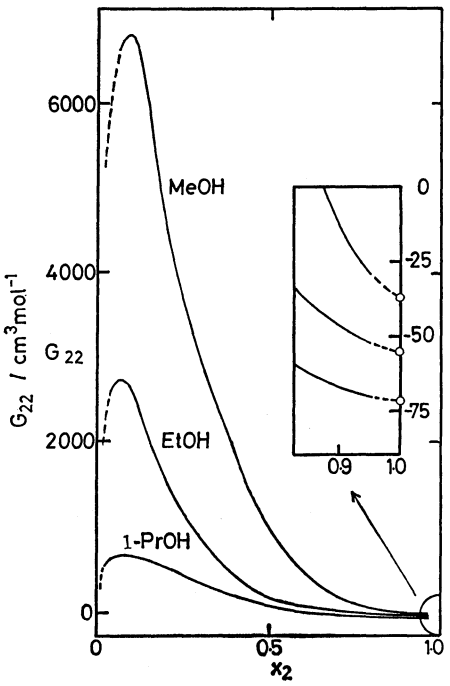

Fig. 4. Concentration dependence of G_{22}.

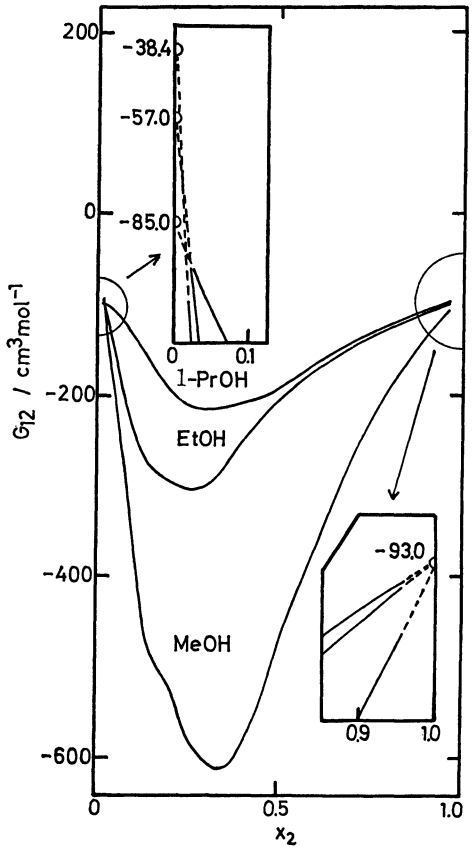

Fig. 5. Concentration dependence of G_{12}.

is reasonable.

Concentration Dependences of G_{11}, G_{22}, and G_{12}. The results shown in Figs. 3—5 may be summarized as follows:

(1) G_{11} is only slightly dependent on the concentration at $x_2<0.1$ especially for the 1-propanol system.

(2) The concentration dependence of G_{11} is similar to that for ordinary binary solutions such as cyclohexane–2,3-dimethylbutane obtained by Dunkersloot.[6]

(3) The magnitudes of G_{22} are much larger than those for ordinary solutions especially in the low concentration range of alcohol and are in the order methanol>ethanol>1-propanol. The magnitude of G_{22} rapidly decreases as the alcohol concentration increases.

(4) G_{12} acquires a minimum value. The magnitudes of the minimum values are in the order 1-propanol>ethanol>methanol.

Interpretation of G_{11}, G_{22}, and G_{12}. Evaluation of the parameters G_{11}, G_{22}, and G_{12} enables us to discuss the solute-solute, solvent-solvent, and solute solvent interactions independently. G_{ij} should be related to the intermolecular interactions and local structures formed in a solution.

It is preferable to discuss the quantity $g_{ij}(r)$ included in G_{ij}, but it cannot be done easily at this stage. Therefore, we will discuss G_{ij} from the standpoint of fluctuations. The parameters G_{11}, G_{22}, and G_{12} can be expressed in terms of the mean numbers of molecules in the volume V, N_1, and N_2, as[24]

$$G_{11} \equiv \int \{g_{11}(r)-1\}\mathrm{d}^3r = v\frac{\overline{N_1^2}-(\overline{N}_1)^2}{(\overline{N}_1)^2} - v_1$$

$$G_{22} \equiv \int \{g_{22}(r)-1\}\mathrm{d}^3r = v\frac{\overline{N_2^2}-(\overline{N}_2)^2}{(\overline{N}_2)^2} - v_2 \qquad (7)$$

$$G_{12} \equiv \int \{g_{12}(r)-1\}\mathrm{d}^3r = v\frac{\overline{N_1N_2}-\overline{N}_1\overline{N}_2}{\overline{N}_1\overline{N}_2}.$$

Equation 7 corresponds to the following relations;

$G_{11}+\bar{v}_1$: number fluctuation of solvent molecules,

$G_{22}+\bar{v}_2$: number fluctuation of solute molecules,

G_{12} : correlation of number fluctuation between solute and solvent molecules.

The large negative value of G_{12} for the alcohol–carbon tetrachloride system indicates the large negative correlation of the number fluctuation between solute and solvent molecules. Similarly, the abrupt increase of G_{22} in the low alcohol concentration range suggests a sudden increase of the correlation between alcohols in the solution. The magnitude of the correlations are in the order methanol>ethanol>1-propanol. On the other hand, G_{11} is slightly dependent on the concentration at $x_2<0.1$. This shows that the structure existing in carbon tetrachloride is held in the solution at the low concentration of alcohol, especially in the case of 1-propanol. These results correspond to the fact that the intermolecular interaction between alcohols is much stronger than that between carbon tetrachlorides in the binary solution of alcohol and carbon tetrachloride.

Concluding Discussion. From the discussion of the preceeding paragraphs the properties of the binary solution of alcohol and carbon tetrachloride may be summarized as follows.

1) The behavior of carbon tetrachloride molecules is not singular but quite normal.

2) All the peculiar properties of the solution come not from the intermolecular interaction between alcohol and carbon tetrachloride, but from the strong interaction between the alcohol molecules as can be seen from the magnitudes of G_{22} and G_{12}.

3) The magnitude of the interactions between the alcohol molecules is in the order methanol>ethanol>1-propanol. For the 1-propanol system, the interaction between the alcohol molecules is weaker.

4) The singular behavior of the alcohol molecules arises from the fact that the alcohol molecules are surrounded by carbon tetrachloride molecules as can be seen from the sharp maximum of G_{22} at low concentrations of alcohol. The above conclusions strongly suggest the formation of a local structure composed of alcohol molecules in the carbon tetrachloride solution. The detailed discussion concerning the local structure formation can be made only when each $g_{ij}(r)$ included in G_{ij} can be quantitatively related to the specific intermolecular interactions in a solution. Work along this line is in progress.

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