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Far-infrared Absorption of Non-dipolar Liquid Mixtures

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Synopsis. Far-infrared absorptions of some non-dipolar liquid mixtures have been observed. The changes of the intensities with mixing ratio were examined on the basis of a formula derived for the difference between absorption intensities before and after mixing, to get information about the mixing state.

The far-infrared absorption of a non-dipolar liquid arises mainly from the bimolecular collisions and thus the absorption of a mixture of the non-dipolar liquids contains valuable information about the mixing state.[1,2] In the present study, the far-infrared absorptions were measured for benzene+cyclohexane, benzene+carbon disulfide, benzene+1,4-dioxane, and carbon disulfide+cyclohexane mixtures. The results were examined by means of a refined formula derived for the difference between the absorption intensities before and after mixing, to get information about the mixing state.

Experimental

The spectral measurements were performed at room temperature with the apparatus described previously.[3] The absorption coefficients were obtained by the equation:

$$\alpha(\nu) = \ln(I_1/I_2)/(l_2 - l_1), \tag{1}$$

where I_1 and I_2 are the transmitted intensities for the two sample thicknesses, l_1 and l_2, respectively. Thus the effects of the surface- and internal-reflection were minimized. The integrated intensities, $A=\int\alpha(\nu)\mathrm{d}\nu$, were estimated in a range from 10 to 220 cm^{-1}, except for samples containing 1,4-dioxane, for which integrations were performed over a range from 10 to 170 cm^{-1}. Spectroscopic grade samples were used for carobn disulfide, benzene, cyclohexane, and 1,4-dioxane. The observed spectra for pure liquids were consistent with the results previously reported.[1,2,4]

Theoretical

If the absorption arises from the bimolecular collisional process[1,2] in addition to the intramolecular process, the absorption intensity for a neat liquid is expressed as follows:

$$A = A_a/v_a + A_{aa}/v_a^2,$$

where v_a is the molar volume and A_a and A_{aa} denote the absorptions due to the intramolecular vibrations and the bimolecular collisions respectively. Let us consider the mixture of a and b components with volume ratio of $x/(1-x)$. The excess volume of mixing is ignored, since it is less than 1 vol % for ordinary organic liquids.[5] The absorption intensity before mixing is provided by the average of those of the neat liquids concerned as follows:

$$A_0 = x(A_a/v_a + A_{aa}/v_a^2) + (1-x)(A_b/v_b + A_{bb}/v_b^2), \tag{2}$$

where subscripts a and b indicate the two components. After mixing, the collision between the different species also takes part in the absorption and the intensity is expressed as follows:

$$\begin{aligned} A_m &= x(A_a/v_a + \varphi_{aa}xA_{aa}/v_a^2) \\ &\quad + (1-x)[A_b/v_b + \varphi_{bb}(1-x)A_{bb}/v_b^2] \\ &\quad + 2x(1-x)\varphi_{ab}A_{ab}/v_av_b, \end{aligned} \tag{3}$$

where φ_{aa}, φ_{bb}, and φ_{ab} are the relative ease of the three types of collision. These quantities represent the mixing state of the mixture. In the case of random mixing, all the three values are equal to unity. In general, however, these values are dependent upon the mixing ratio and are different from each other. They can probably be replaced by the probabilities of the intermolecular bond formation. Then the number ratio of the three types of bond, a–a, b–b, and a–b, is given by $f^2\varphi_{aa}:(1-f)^2\varphi_{bb}: 2f(1-f)\varphi_{ab}$, where f is the mole fraction of component a. According to Schulze,[6] these values are interrelated as follows:

$$\varphi_{ab} = \varphi, \quad \varphi_{aa} = \frac{1-\varphi+\varphi f}{f}, \quad \varphi_{bb} = \frac{1-\varphi f}{1-f}. \tag{4}$$

Since φ_{aa}, φ_{bb}, and φ are all positive, $0<\varphi<\min(f^{-1}, (1-f)^{-1})$. Besides, the limit of $\varphi(f)$ is unity as f approaches 0 or 1. The relationships among f, x, and the number of moles in unit volume, N, are $f=v_bx/[v_bx+v_a(1-x)]$, and $N=[fv_a+(1-f)v_b]^{-1}$. From Eqs. 2, 3, and 4 the difference between the absorption intensities before and after mixing is given by

$$\begin{aligned} \Delta A_m &= A_m - A_0 \\ &= -N^2f(1-f)[(\varphi+v_b/v_a-1)A_{aa} \\ &\quad + (\varphi+v_a/v_b-1)A_{bb} - 2\varphi A_{ab}]. \end{aligned} \tag{5}$$

Hereafter, ΔA_m is referred to as the absorption of mixing, by analogy with the heat of mixing.

In the case of random mixing, in which the φ value is unity, Eq. 5 becomes:

$$\Delta A_m = -Cf(1-f)[fv_a + (1-f)v_b]^{-2}, \tag{6}$$

where

$$C = (v_b/v_a)A_{aa} + (v_a/v_b)A_{bb} - 2A_{ab}.$$

If the molar volumes of the components are equal, *i.e.*, $v_a=v_b$, the f-dependence of ΔA_m is simply parabolic.

Results and Discussion

The integrated intensities obtained are plotted against the mole fraction f in the upper parts of Fig. 1(a—d). The standard errors for spectral measurements are indicated by the vertical bars. The solid line shows the intensity before mixing, A_0. For a mixture of two components with different molar

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volumes, the mole fraction is nonlinear to the volume fraction. The molar volumes of benzene, cyclohexane, carbon disulfide, and 1,4-dioxane are 88.9, 108.1, 60.3, and 85.2 cm^3/mol, respectively. Then the A_0 curve for the benzene+1,4-dioxane mixture is almost straight, whereas that for the carbon disulfide+cyclohexane mixture shows the largest deviation from a straight line.

The absorptions of mixing, ΔA_m, are shown in the lower parts of Fig. 1(a—d) on an expanded scale. As may be seen in Eq. 5, the absorptions due to the monomolecular processes, A_a and A_b, are cancelled out in ΔA_m. Thus the intramolecular vibrational bands, such as the bands at 150 cm^{-1} of 1,4-dioxane and at 240 cm^{-1} of cyclohexane, contribute little to the values of ΔA_m. The broken lines in Fig. 1 show the values calculated from Eq. 6 with C values adjusted. For the benzene+cyclohexane and benzene+carbon disulfide mixtures, good fits were obtained between the observed and calculated values of ΔA_m. Therefore, the condition of random mixing may hold for these mixtures. The sign of ΔA_m for the benzene+cyclohexane mixture is negative, whereas that for the benzene+carbon disulfide mixture is positive. For the a+b mixture, the sign of ΔA_m is determined by the sign of C, *i.e.*, $(v_b/v_a)A_{aa}+(v_a/v_b)A_{bb}-2A_{ab}$. For the benzene+cyclohexane system, the molar volumes of the two components, v_a and v_b, are approximately equal and the benzene–benzene absorption, A_{aa}, is much stronger than the cyclohexane–cyclohexane absorption, A_{bb}. Therefore, the positive value of C shows that A_{aa} is the dominant absorption. For the benzene+carbon disulfide system, the negative value of C means that A_{ab} is larger than the average of A_{aa} and A_{bb}, which is approximately equal to that of $(v_b/v_a)A_{aa}$ and $(v_a/v_b)A_{bb}$. Davies and Chamberlain[2] considered that the positive sign of ΔA_m was due to a complex or sticky collision interaction between different species. However, as mentioned above, the sign of ΔA_m depends upon the magnitudes of the three types of binary absorption, A_{aa}, A_{bb}, and A_{ab}, which does not necessarily represent directly the strength of the intermolecular bondings.

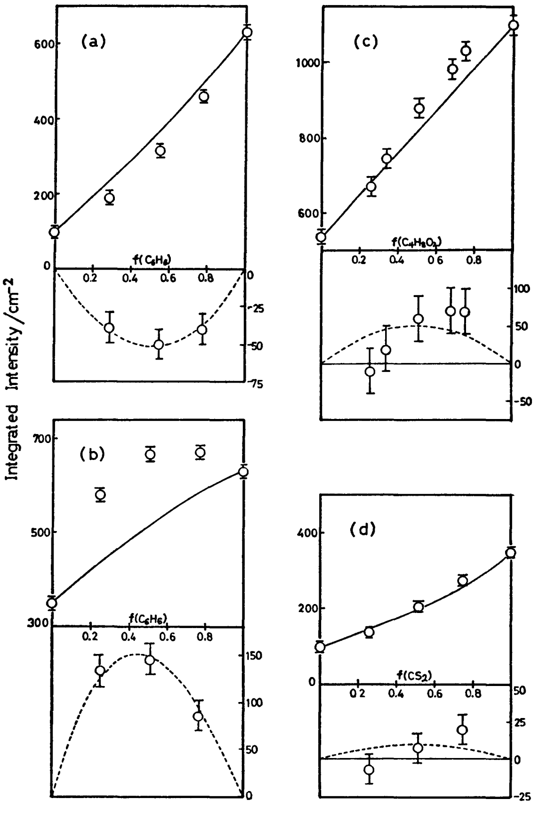

Fig. 1. The mole fraction dependency of the integrated absorption intensity (the upper part) and the absorption of mixing (the lower part) of liquid mixtures:
(a) benzene+cyclohexane,
(b) benzene+carbon disulfide,
(c) benzene+1,4-dioxane,
(d) carbon disulfide+cyclohexane.
The vertical bars indicate the standard errors. The solid lines represent the intensities before mixing. The broken lines represent the values calculated from Eq. 6 with the adjusted C values.

For the benzene+1,4-dioxane and carbon disulfide+cyclohexane mixtures, the observed values of ΔA_m seem to deviate from a symmetrical parabolic curve. Because of a moderately strong interaction between benzene and 1,4-dioxane,[7] the value of φ may change with mole fraction and cause the deviation from the random mixing model.[6] On the other hand, if the absorption due to trimolecular collisions is taken into account, the analytical form for the absorption of mixing will contain a term which has its maximum at f=2/3 or 1/3. This term might also bring about the asymmetry of the ΔA_m curve. Although, at the present stage, it is not clear how much the trimolecular collision contributes to the absorption, it seems probable that the trimolecular absorption is considerably smaller than the bimolecular absorption[8] and that the main features of ΔA_m curve are governed by the latter. Then the deviation in the f-dependence of ΔA_m from Eq. 6 may be ascribed to the deviation in the mixing state from the random mixing. In order to get further insight into the mixing state, theoretical studies about the f-dependence of φ are needed.

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