The Mutual Interaction between Solutes in Gas Chromatography

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In principle, it is expected that the solutes will interact with each other in the liquid phase and that the retention volume of one component will be affected by the presence of the other components. In gas chromatography (gas-liquid partition gas chromatography), howevr, it is generally accepted that solutes do not, in fact, interact with each other in the liquid phase and that the retention volume of one solute is independent of the presence of the other components, because the concentration of each component is infinitely small. In order to elucidate the above problem, a theoretical consideration of the problem will be made from the standpoint of strictly regular solutions, and also a little experimental evidence will be given.

Theoretical Considerations

In considering the effect of the presence of other components on the retention volume of one particular component, the partial vapor pressure of the one component, which relates to its partition coefficient, in the presence of the other component must first be considered. We consider two kinds of components 1 and 2 in samples as solutes and the liquid of the stationary phase as the solvent, and we regard the portion of the stationary phase liquid in which solutes 1 and 2 are dissolved as a uniform ternary system. The system is composed of N_1 molecules of solute 1, N_2 molecules of solute 2, and N_s molecules of the solvent; for the sake of simplicity, it is also assumed that solutes 1 and 2 and the solvent have the same molecular sizes and that these molecules are arranged in $(N_1+N_2+N_s)$ sites of a quasi-crystalline lattice with z nearest neighbors. For zeroth approximation, the configurational free energy F_c of the system is given by

$$F_c=\frac{1}{2}z(N_1+N_2+N_s)\left\{\frac{N_s^2}{(N_1+N_2+N_s)^2}u_{ss}+2\frac{N_sN_1}{(N_1+N_2+N_s)^2}u_{s1}+2\frac{N_sN_2}{(N_1+N_2+N_s)^2}u_{s2}+\frac{N_1^2}{(N_1+N_2+N_s)^2}u_{11}+\frac{N_2^2}{(N_1+N_2+N_s)^2}u_{22}+2\frac{N_1N_2}{(N_1+N_2+N_s)^2}u_{12}\right\}+\boldsymbol{k}T\left(N_s\ln\frac{N_s}{N_1+N_2+N_s}+N_1\ln\frac{N_1}{N_1+N_2+N_s}+N_2\ln\frac{N_2}{N_1+N_2+N_s}\right) \quad (1)$$

where u_{ij} denotes the mutual interaction energy of the ij pair, $\boldsymbol{k}$ is the Boltzmann constant, and T is the absolute temperature. The chemical potential of solute 1 in the liquid phase, $\mu_1{}^l$ can be obtained by differentiating Eq. 1 with respect to N_1. $\mu_1{}^l$ is then expressed as

$$\left(\frac{\partial F_c}{\partial N_1}\right)=\mu_1{}^l=-x_s{}^2u_{ss}+2x_s(1-x_1)u_{s1}-2x_sx_2u_{s2}+x_1(2-x_1)u_{11}-x_2{}^2u_{22}+2x_2(1-x_1)u_{12}+\boldsymbol{k}T\ln x \quad (2)$$

where x_s, x_1 and x_2 denote $N_s/(N_1+N_2+N_s)$, $N_1/(N_1+N_2+N_s)$ and $N_2/(N_1+N_2+N_s)$ respectively. If we define the quantities w_{s1}, w_{s2} and w_{12} as

$$\left.\begin{aligned}w_{s1}&=2u_{s1}-u_{ss}-u_{11}\\w_{s2}&=2u_{s2}-u_{ss}-u_{22}\\w_{12}&=2u_{12}-u_{11}-u_{22}\end{aligned}\right\} \quad (3)$$

and use the relation that $x_1+x_2+x_s=1$, Eq. 2 can be rewritten as

$$\mu_1{}^l=x_{s2}w_{s1}+x_2{}^2w_{12}+x_2x_s(w_{12}+w_{s1}-w_{s2})+u_{11}+\boldsymbol{k}T\ln x_1 \quad (4)$$

Similarly, the chemical potential of Solute 2, $\mu_2{}^l$, is given by

$$\mu_2{}^l=x_s{}^2w_{s2}+x_1{}^2w_{12}+x_1x_s(w_{12}-w_{s1}+w_{s2})+u_{22}+\boldsymbol{k}T\ln x_2 \quad (5)$$

For the gas phase, the solute molecules are assumed to be perfect and to have no interaction with other molecules. Therefore, if we neglect the contribution of the internal degrees of freedom to the chemical potential, the chemical potentials of solutes 1 and 2, $\mu_1{}^g$ and $\mu_2{}^g$ respectively, are given by:

$$\mu_1{}^g=\boldsymbol{k}T\ln N_1{}^g/V \quad (6)$$

$$\mu_2{}^g=\boldsymbol{k}T\ln N_2{}^g/V \quad (7)$$

where $N_1{}^g$ and $N_2{}^g$ denote the number of molecules of solutes 1 and 2 respectively in the gas phase of volume V. In equilibrium, the chemical potential of each species is equal in both the liquid and gas phases; therefore, by equating 4 with 6 and 5 with 7, the following relations are obtained;

$$\boldsymbol{k}T\ln N_1{}^{g}/V=x_s{}^2w_{s1}+x_2{}^2w_{12}+x_2x_s(w_{12}+w_{s1}-w_{s2})+u_{11}+\boldsymbol{k}T\ln x_1 \tag{8}$$

$$\boldsymbol{k}T\ln N_2{}^{g}/V=x_s{}^2w_{s2}+x_1{}^2w_{12}+x_1x_s(w_{12}-w_{s1}+w_{s2})+u_{22}+\boldsymbol{k}T\ln x_2 \tag{9}$$

Since the partition coefficient is the ratio of the mumber of solute molecules in the unit volume of the stationary liquid phase to that in the gas phase, the partition coefficient of solute 1, $k_1{}^{m}$, and that of solute 2, $k_2{}^{m}$, for their mixture are given by:

$$\begin{aligned}\ln k_1{}^{m}&=\ln N_1x_1-\ln N_1{}^{g}/V\\&=-(1/\boldsymbol{k}T)\cdot\{x_s{}^2w_{s1}+x_2{}^2w_{12}+x_2x_s(w_{12}+w_{s1}-w_{s2})+u_{11}\}\end{aligned} \tag{10}$$

$$\begin{aligned}\ln k_2{}^{m}&=\ln N_1x_2-\ln N_2{}^{2}/V\\&=-(1/\boldsymbol{k}T)\cdot\{x_s{}^2w_{s2}+x_1{}^2w_{12}+x_1x_s(w_{12}-w_{s1}+w_{s2})+u_{22}\}\end{aligned} \tag{11}$$

where N_1 is the number of molecules in the unit volume of the stationary liquid phase. The partition coefficients $k_1{}^{o}$ and $k_2{}^{o}$ for the pure solutes 1 and 2 respectively are obtained by equating x_2 or x_1 in Eqs. 10 and 11 with zero and are given by:

$$\begin{aligned}\ln k_1{}^{0}&=\ln N_1x_{10}-\ln N_1{}^{g}/V\\&=-(1/\boldsymbol{k}T)\cdot(x_{s1}{}^2w_{s1}+u_{11})\end{aligned} \tag{12}$$

$$\begin{aligned}\ln k_2{}^{0}&=\ln N_1x_{20}-\ln N_2{}^{g}/V\\&=-(1/\boldsymbol{k}T)\cdot(x_{s2}{}^2w_{s2}+u_{22})\end{aligned} \tag{13}$$

where x_{10} and x_{20} denote the mole fraction of solutes 1 and 2 respectively, and x_{s1} and x_{s2} denote the corresponding mole fraction of the solvent when only a single solute is present. From Eqs. 10, 11, 12 and 13 the ratio of partition coefficients for the mixture to that for the pure component, when there is an equal concentration in the stationary liquid phase, that is, $x_{10}=x_1$ and $x_{20}=x_2$, $k_1{}^{m}/k_1{}^{o}$ and $k_2{}^{m}/k_2{}^{o}$, are given by using the relation $x_{s1}=x_s+x_2$ or $x_{s2}=x_s+x_1$:

$$\ln k_1{}^{m}/k_1{}^{o}=-(1/\boldsymbol{k}T)\cdot\{x_2{}^2(w_{12}-w_{s1})+x_2x_s(w_{12}-w_{s1}-w_{s2})\} \tag{14}$$

$$\ln k_2{}^{m}/k_2{}^{o}=-(1/\boldsymbol{k}T)\cdot\{x_1{}^2(w_{12}-w_{s2})+x_1x_s(w_{12}-w_{s1}-w_{s2})\} \tag{15}$$

Generally, the right sides of Eqs. 14 and 15 are not equal to zero, and $k_1{}^{m}$ and $k_2{}^{m}$ differ from $k_1{}^{o}$ and $k_2{}^{o}$ respectively; consequently, the retention volume for the mixture differs from that for the pure component.

Experimental

The experiments were performed for the equivolume mixture of chloroform-ethyl methyl ketone with a column of apiezon J and those of the chloroform-carbon tetrachloride and chloroform-toluene mixture with a column of P. E.; also, the position of each peak was compared with that obtained for the pure substances. In this case the quantity of each component was kept equal. The results obtained are shown in Table I.

Discussions

If $x_2\ll 1$, and $x_1\ll 1$, x_s is approximated to be equal to 1, and the term containing $x_1{}^2$ or $x_2{}^2$ is neglected as too small, and if, in expanding the exponential function, the terms higher than the second are also neglected, Eqs. 14 and 15 can be approximated as

$$k_1{}^{m}=k_1{}^{o}\{1-(1/\boldsymbol{k}T)\cdot x_2(w_{12}-w_{s1}-w_{s2})\} \tag{16}$$

TABLE I. COMPARISON OF THE RETENTION TIME FOR MIXTURES ($T_r{}^{m}$) WITH THAT FOR PURE COMPONENTS ($T_r{}^{o}$). (The quantity of each component is 25μl.)

Sample	$T_r{}^{o}$, min.	$T_r{}^{m}$, min.	ΔT_r, min.	$\Delta T_r/T_r{}^{o}$
Ethyl methyl ketone	7.60	7.83	0.23	0.030
Chloroform	10.95	11.63	0.68	0.062

Experimental Conditions —— Temp.: 52°C; Press.: 34.75 mmHg; Column: Cu pipe; Stationary phase: Apiezon J 420 g.; Support: C·22; Firebrick: 1200 g. 42～60 mesh; Carrier gas: H_2; Flow rate: 94 cc./min.

Sample	$T_r{}^{o}$, min.	$T_r{}^{m}$, min.	ΔT_r, min.	$\Delta T_r/T_r{}^{o}$
Carbon tetrachloride	4.55	4.64	0.10	0.022
Chloroform	10.16	10.35	0.19	0.019

Experimental conditions —— Temp.: 70.2°C; Press.: 26.2 mmHg; Column: Cu pipe 4 m; Stationary phase: P. E. G. 3; Support: Celite 10; Carrier gas; H_2; Flow rate: 77 cc./min.

Sample	$T_r{}^{o}$, min.	$T_r{}^{m}$, min.	ΔT_r, min.	$\Delta T_r/T_r{}^{o}$
Toluene	13.74	14.02	0.26	0.019
Chloroform	8.97	9.05	0.08	0.009

Experimental conditions —— Temp.: 70.2°C; Press.: 31.0 mmHg; Flow rate: 83 cc./min; Other conditions were the same as above.

$$k_2^{m}=k_2^{o}\{1-(1/kT)\cdot x_1(w_{12}-w_{s1}-w_{s2})\} \quad (17)$$

These equations show that the effect of interaction with a foreign substance is proportional to its concentration.

It may also be inferred that the partition coefficient in the mixture increases or decreases as the sign of $(w_{12}-w_{s1}-w_{s2})$ is positive or negative. This indicates that the position of the peak for a particular component is shifted to either the shorter or longer side according to the kind of other component in the mixture.

In the above discussions, it is tacitly assumed that the two solutes coexist and that the concentration of each solute does not change with time. However, in actuality, the concentration of each solute changes with time and the two solutes are gradually separated as they proceed through a column and are finally completely separated where the effect of interaction with the other solute does not occur. This means that the k_1^{m}/k_1^{o} or k_2^{m}/k_2^{o} ratio changes with time, even if the two solutes are always both present, if not, its value approaches 1 when the two solutes are completely separated. The time required for the value of k_1^{m}/k_1^{o} or k_2^{m}/k_2^{o} to reach 1 is dependent on the kind of solute. If the retention times of solutes 1 and 2 are denoted by T_1 and T_2 respectively, the effect of the interaction becomes larger as T_1/T_2 approaches 1.

The assumption that the solute and the solvent have the same molecular size is far from the actual case, for the molecular size of the stationary liquid phase is of an order ten times greater than that of most samples. However, the effect of the difference in molecular size is not significant if the mole fractions in the expressions are replaced by the volume fractions.

As for the experimental results, in the mixture of chloroform (1) and ethyl methyl ketone (2) it was found that the component peaks shifted to a positive direction compared with those for single component samples when an apiezon J column is used. This is interpreted as follows: the heat of the mixing of chloroform with ethyl methyl ketone may be negative, since the two components may form a hydrogen-bonded complex as chloroform and acetone do; hence, the value of w_{12} may be negative.

Further, since both component molecules, 1 and 2, have dipoles and since the stationary phase liquid apiezon J(s) is a homologue of aliphatic hydrocarbons, the heats of the mixing of s with 1 and with 2 may both be positive and the values of w_{s1} and w_{s2} may be positive. Accordingly, the value $(w_{12}-w_{s1}-w_{s2})$ in Eqs. 16 and 17 may be negative; it therefore follows that $k_1^{m}>k_1^{o}$ and $k_2^{m}>k_2^{o}$ and the position of each component peak in the mixture may be shifted in the positive direction. This prediction coincides with the experimental results. An example of the reverse case, in which the relation $k_1^{m}<k_1^{o}$ and $k_2^{m}<k_2^{o}$ holds, has not yet been found.

For a quantitative discussion of this problem we must further derive those expressions which relate the concentration of the single component sample in the column with the time which has transpired after the sample injection under the assumption that the partition coefficient of each component varies with its concentration in the column; then we must integrate the contribution due to mutual interaction at each concentration. Further, the same procedure must be repeated for the mixture samples and the latter results compared with the former. We do not intend to deal with this problem here.

Theory predicts that the shift of each component peak due to mutual interaction will occur in the same direction. The experimental results coincide with this prediction.

It should be noted that an apparent shift in the two peaks occurs when they approach, but that the directions of the shifts are such that the two peaks come close together and are opposite each other, which effect can easily be discriminated from what originates from the mutual intearction.

Although in the present experiment a considerable quautity of samples (25 μl.) was used, the relative shift of the peaks was 6% at most, which wonld be a much smaller value if much smaller quantity of samples were used. In actuality, the quantity of samples is usually of an order of a few μl. and the effect of mutual interaction can be neglected. However, when the minor component is analysed by using large amount of the sample, the effect may become important.

Summary

The influence of the mutual interaction between the molecules of different components in the sample on the retention volume of each component has been discussed from the standpoint of a strictly regular solution. The retention volume of each component in the mixture either increases or decreases, compared with that in the single component samples, according to the kinds of sample and of stationary phase liquid.

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