Study on the Vapor Gas Emissions from Chemical Tanker During Benzene Loading Operation

by

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Abstract

International Maritime Organization (IMO) recognized that chronic exposure to benzene vapors in air may cause leukemia even if the concentration is very low, such as a few parts per million. To predict the exposure level of crews, it is necessary to investigate the actual conditions of vapor emission from chemical tankers engaged in benzene transfer operation. Since it is difficult to realize experiments using actual chemical tanker in service, scale model experiment was conducted to estimate the concentration of benzene gas emitted during loading operation. The dimensions of the scale model tank used for the experiments are 0.89m in length, 0.39m in breadth and 0.44m in depth. It is a 1/10 scale of the typical cargo tank placed on the 499 Gross Tonnage chemical tanker which is usually used for benzene transportation in Japan.

Three factors affecting the concentration of benzene gas emitted during loading operation are found from the scale model experiments. Primary mechanism of diffusion is one-dimensional molecular diffusion advancing in the vertical direction. The others are eddy diffusion above surface in the initial period of the loading operation and advection under the tank ceiling. A new calculation method including three mechanisms was developed and the result of calculation was compared with the data obtained from onboard measurement. It is found that calculation method described in this paper can predict the concentration of benzene gas emitted during loading operation in terms of order estimation.

1. Introduction

Many kinds of and large amount of chemicals are produced in the world. We can't consider current human prosperity without research and development on new chemicals. However, the adverse effect of chemicals against the human health is focused on these days. Especially, benzene is recognized as human carcinogen and it is categorized into the class 1 by IARC (International Agency for Research on Cancer). Class 1 indicates the strongest correlation with carcinogencity in humans. However, benzene is fundamental material to make some types of pesticide, paint, medicine, glue and so on. Therefore, large amount of benzene, over 4 million tonnage one year, is produced and more than one million tonnage of benzene is transported by chemical tankers in Japan.

The 499 Gross Tonnage chemical tanker is often used for the benzene transfer in Japan. Figure 1 shows the schematic view of this chemical tanker. The benzene gas evaporates on the surface of liquid benzene in cargo tank during loading operation and high concentration gas is emitted from vent post into the atmosphere. The health condition of crews and dock workers around chemical tanker during loading operation is worried, because it is recognized that chronic

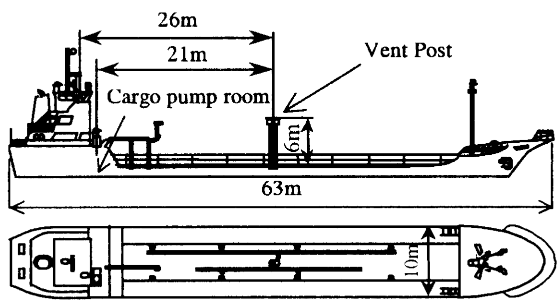

Fig.1 499 Gross Tonnage Chemical Tanker

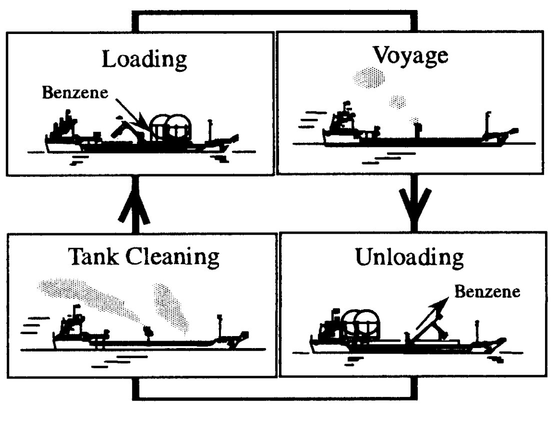

Fig.2 Benzene Transfer Cycle

exposure to benzene vapors in air may cause leukemia even if the concentration is very low, such as a few parts per million. We conducted onboard measurements to obtain the benzene concentration in whole transfer operation to estimate working environment level[1]. Figure 2 shows benzene transfer cycle composed of four operations, loading, transit, unloading and tank cleaning.

The first operation of the cycle is loading operation. The liquid benzene is loaded at the marine terminal of refinery producing liquid benzene. The benzene gas evaporating on the surface of liquid phase in cargo tank is emitted from the vent post located at the center on the weather deck.

The second operation is navigation. When the pressure of ullage space in cargo tank exceeds the pressure set point, the pressure vacuum valve opens to release the gas until the pressure reduces below its set point.

The third operation is unloading operation. The liquid benzene is unloaded by the cargo pump integrated in the chemical tanker. Air is drawn into cargo tanks during this operation. Therefore, if there is no leakage of the cargo pump, the manhole and the ullage hatch then the concentration of benzene should be low level.

The fourth operation is tank cleaning. After unloading operation, cargo tanks are cleaned by air supplied from a blower to avoid the contamination caused from the mixture between benzene and next cargoes. The largest amount of benzene gas in the transfer cycle is emitted during this operation. The source of benzene gas is the residues of liquid benzene adhering to tank walls, bottom and ceiling due to its interfacial tension and viscosity.

Our final purpose is to evaluate the exposure level in the whole transfer operation indicated in this cycle. In this paper, we focus on the loading operation. Since loading operation is carried out at the marine terminal of refinery, more workers than another operations have a potential to be exposed to the high concentration of benzene gas.

We investigated the concentration of benzene gas emitted from chemical tankers during loading operation several times. It is found from these measurements that the concentration varies with the surface level of liquid benzene in the cargo tank. The concentration increases sharply after the surface level exceeds the half of the tank depth. The density of benzene gas is about three times larger than that of air or nitrogen in the

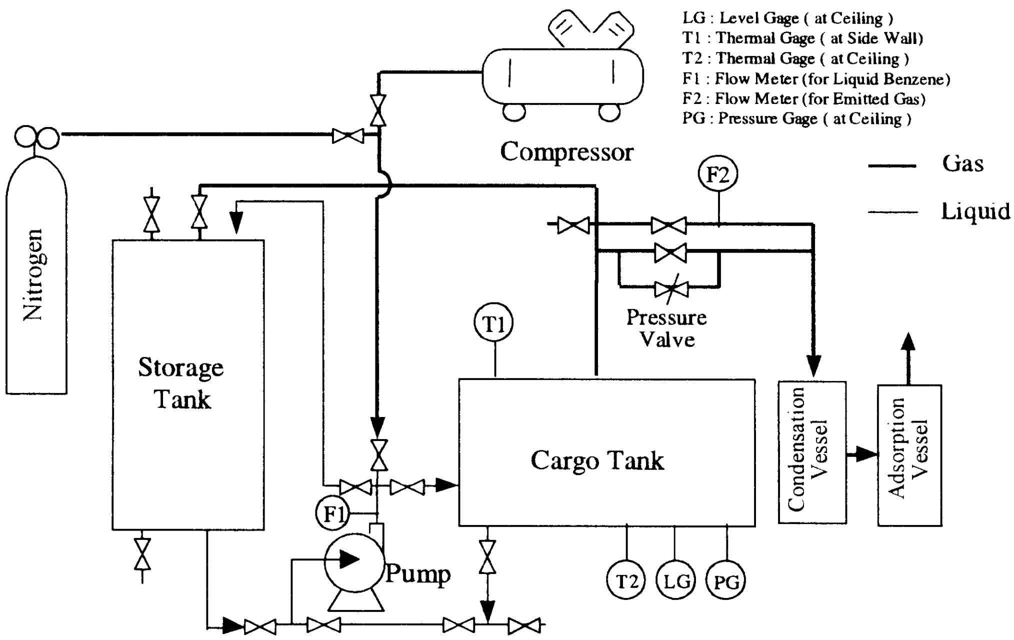

Fig.3 Schematic Diagram of the Scale Model of Cargo Tank

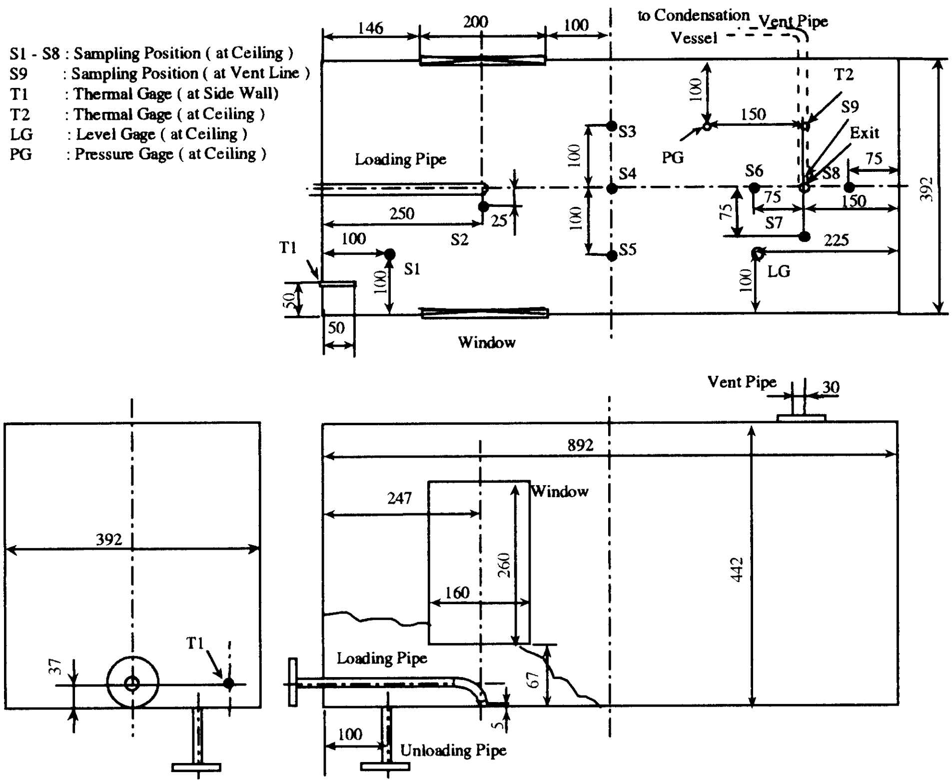

Fig.4 Scale model of Cargo Tank (Unit: mm)

tank. (Cargo tank is sometimes filled with nitrogen to avoid a detonation.) Benzene gas stratifies above the surface of liquid benzene. The concentration of emitted benzene gas increases rapidly when this layer closes to the ceiling of the cargo tank. The calculation method by one-dimensional molecular diffusion advancing in the vertical direction is given in the section 5.1 in this paper. The difference between measurement and this calculation is large. This phenomenon implies that eddy diffusion or advection occurred in the cargo tank. However, it is difficult to conduct experiments to grasp the mechanism of diffusion in cargo tank using chemical tankers in service. We carried out experiments with 1/10 scale model of the cargo tank and it is found from the results that diffusion phenomenon in the cargo tank during loading operation has three factors. Considering these factors, a calculation method to estimate the time history of concentration of vapors displaced during benzene loading operation was developed and its detail is described in the following chapters. There are some calculation models to estimate the emission amount of crude oil or gasoline vapors [2]. However, these models are composed of empirical equations not to be induced from the considerations on physical properties. Thus, a new calculation model involving these properties is needed to estimate the emission quantity of benzene and the calculation method in this paper is taking account of physical properties and the effect of both eddy diffusion and advection.

2. Instruments and Measurement Method

Figure 3 shows the schematic diagram of the equipment used for the scale model experiments. Before conducting the experiment, the cargo tank was cleaned by air supplied from the compressor to reduce the concentration of benzene to the order of 1ppm. After this process, the tank was filled with nitrogen to avoid explosion. Liquid benzene was loaded into the cargo tank from the storage tank through a diaphragm pump. The top view, the front view and the side view of the scale model of cargo tank are illustrated in Figure 4. The dimensions of the tank used for the experiments are 0.89 (m) in length, 0.39 (m) in breadth and 0.44 (m) in depth. This model tank is a 1/10 scale of typical cargo tank placed on the 499 gross tonnage chemical tanker in Japan. There are sampling holes at the ceiling (S1-S8) and at the vent pipe (S9). The temperature, the pressure, and the surface level in the cargo tank and the flow rate were measured throughout the experiments by the apparatuses indicated in this figure.

A sampling tube which diameter is about 1 (mm) was inserted into the sampling hole and the gas in the tank was sampled by the syringe connected to the end of sampling tube. Only 2 (mL) sampled gas in the syringe was injected into the collecting bottle which volume was 1000(mL). The collecting bottle was vacuumed prior to the injection of sampled gas. Subsequently, the gas in the bottle was diluted with air and analyzed by a gas chromatography with flame ionization detector (FID).

3. Experiments

3.1 Onboard Measurement

To obtain the concentration of benzene gas emitted from a cargo tank during benzene loading operation, onboard measurements were conducted. Figure 5 illustrates the schematic of the method to sample the emission gas. A teflon tube was inserted into the drain cock attached at the root of the vent post. Another end of the sampling tube is connected to the cock of a depressed collecting bottle. The emission gas was sampled by opening these cocks when surface level in the cargo tank reached to some level. This procedure was repeated several times with changing the sampling bottle and subsequently, the concentration of benzene in the sampled gas was analyzed by a gas chromatography.

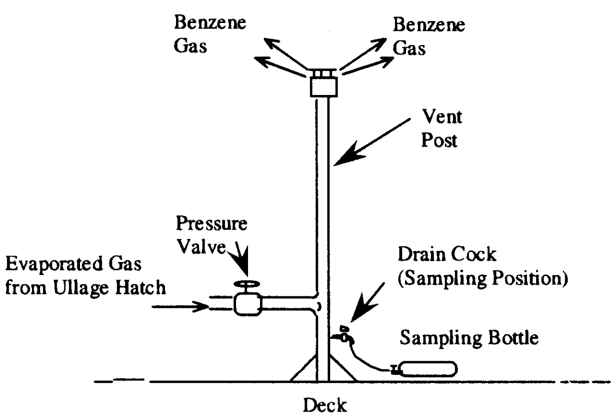

Fig.5 Schematic of sampling method onboard

3.2 Experiments with Scale Model

The mechanism of diffusion in cargo tank can be separated into three factors as follows.

(1) Initial period of the loading, liquid surface level is low enough to disturb the gas phase above the surface. The eddy diffusion caused by this disturbance makes large concentration flux on the surface.

(2) After the surface height of liquid benzene reaches some level at which intensity of the disturbance of the liquid surface is too small to affect on the concentration flux owing to the viscosity of liquid benzene. Diffusion phenomenon is dominated by the one-dimensional molecular diffusion in the vertical direction during this period.

(3) The difference of the cross-sectional area between the cargo tank and that of the vent pipe is very large. Therefore, the flow pattern around the part of connection between the cargo tank and the vent pipe forms three-dimensional structure as shown in Figure 9. This effect indicates that advection occurs in this region and large concentration above surface is transported to the inlet of the vent line when the surface of liquid benzene closes to the tank ceiling.

Two experiment methods were employed to separate the factors of diffusion mechanism in the cargo tank described above.

3.2.1 Experiment Method for Advection under Tank Ceiling (Loading Method)

One of two experimental methods is ordinary loading method. Liquid benzene was loaded into the cargo tank from storage tank. The difference of concentration between at the tank top and in the vent pipe was measured for analysis of the third factor of diffusion mechanism, advection under the ceiling described above.

3.2.2 Experiment Method for Eddy diffusion above Liquid Surface (Circulation Method)

The surface level was kept on a low level by circulating the liquid benzene in the cargo tank through the diaphragm pump without supplying another benzene from storage tank in Figure 4. The condition and concentration flux at the liquid surface were maintained and became steady state condition by this method (Hereinafter, "Circulation Method"). Time history of concentration profile in the cargo tank was compared and evaluated for the first factor of diffusion mechanism, eddy diffusion above liquid surface described above.

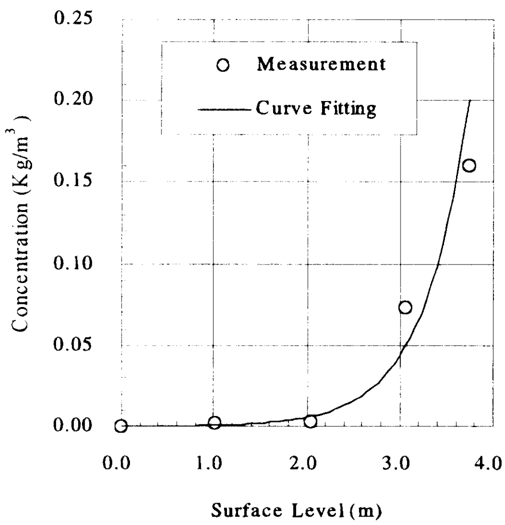

Fig.6 Concentration Profile during Benzene Loading Operation

4. Results of Experiments

4.1 Result of Onboard Measurement

Table.1 shows the experimental condition. Figure 6 shows the relationship between the surface level of liquid benzene and the concentration of benzene gas expelled from one of the eight cargo tanks placed on a 499GT chemical tanker.

Before the surface level reaches to about 70% of the tank depth, the concentration is very low. After that, it increases sharply and final concentration is the order of saturated concentration. Amount of emission from only this cargo tank is estimated to 3.5 (kg) by integrating this concentration profile along with the horizontal axis.

Table.1 Condition of Onboard Measurement

Loading Quantity (kL)	132
Flow Rate (kL/hr)	144
Loading Time (min)	55
Air Temp. (Celsius Degree)	16-24
Cargo Temp. (Celsius Degree)	26
Tank Dimension, L x B x D (m)	7.1 x 5.0 x 4.0

4.2 Results of Experiments with Scale Model

4.2.1 Results of Loading Method

The results of ordinary loading method are shown in Figure 7. These results indicate the relationship between the surface level non-dimensionalized by the tank depth and the concentration of benzene gas divided by the saturate concentration. Since sampling position is in the vent pipe, this value of concentration indicates the concentration of the gas emitted from cargo tank during loading operation. The solid lines in these figures are results obtained from molecular diffusion analysis in the section 5.1. The discrepancy between the experimental data and result of molecular diffusion analysis becomes large with the decrease of the loading flow rate in the higher range of S/D_T. This phenomenon can be considered that the thickness of boundary layer of the gas velocity in the horizontal direction under the ceiling of cargo tank becomes large with the decrease of the flow rate. Figure 9 shows the schematic for this phenomenon.

4.2.2 Results of Circulation Method

Figure 8 shows the results of circulation method. These figures indicate the relationship between the height from liquid surface non-dimensionalized by the tank depth and the concentration of gas divided by saturate concentration at the atmospheric temperature. Since the temperature in the storage tank and cargo tank in Figure 4 was not controlled, the temperature of liquid benzene was equal to the

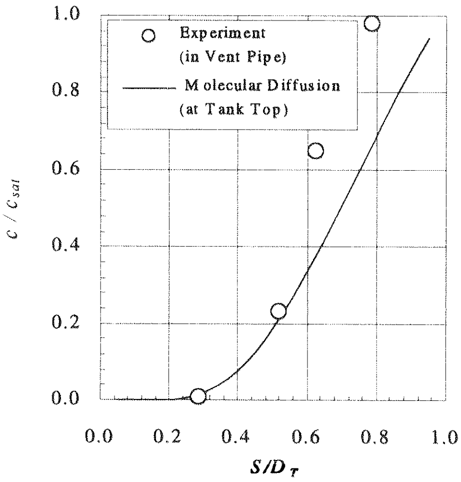

Fig.7.1 Flow Rate= 3.2 (L/min.)

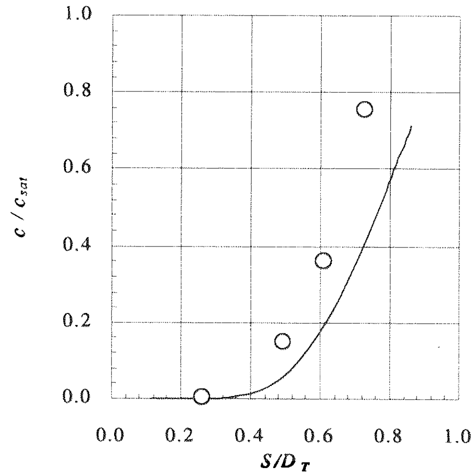

Fig.7.2 Flow Rate= 6.5 (L/min.)

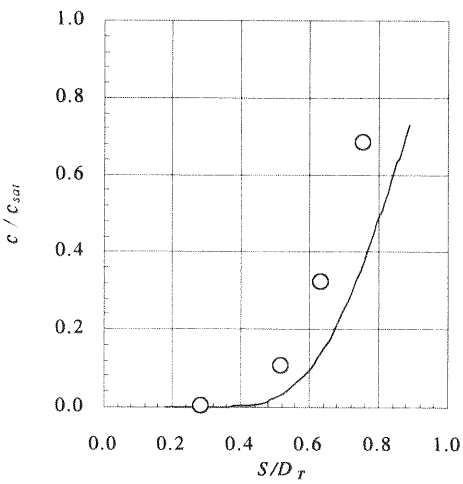

Fig.7.3 Flow Rate= 9.0 (L/min.)

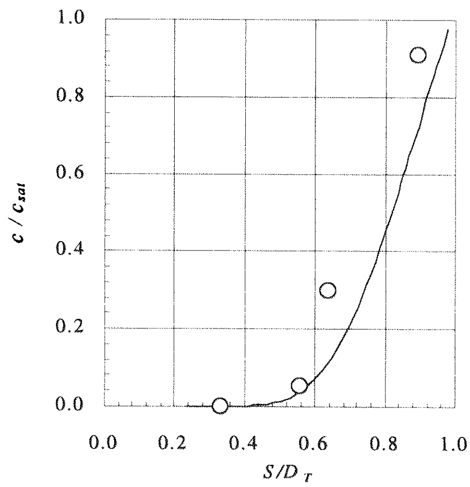

Fig.7.4 Flow Rate= 12 (L/min.)

Fig. 7 Results of Ordinary Loading Method: Solid lines are results of calculation obtained from the calculation method given in Section 5.1, one-dimensional molecular diffusion. The difference between experimental data and molecular diffusion becomes large with decrease of the flow rate.

atmospheric temperature. The solid lines in these figures are obtained by analysis of one-dimensional molecular diffusion described in the section 5.1. When the surface level was maintained at 11 (mm) by circulating liquid benzene between the pump and the model tank, the concentration profiles agreed with the results obtained from molecular diffusion. However, in the case of 6 (mm), the concentration becomes larger than that of molecular diffusion. This difference is caused by the eddy diffusion of gas above the liquid surface. When the height of liquid surface is low, the surface is agitated by the momentum energy of the liquid benzene entering into the cargo tank through the inlet of loading line. This agitation propagates to the gas phase above surface and eddy diffusion forms larger concentration flux than that of molecular diffusion. But this period is too short for the scale model of cargo tank to affect the concentration distribution formed by ordinary loading method.

5. Modeling

5.1 One-Dimension Molecular Diffusion

One-dimension molecular diffusion advancing in the vertical direction is based on the

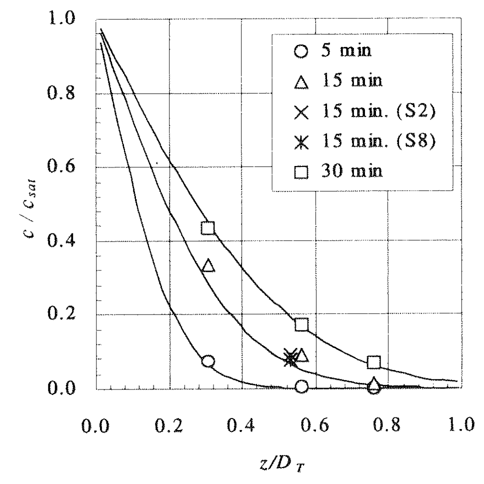

Fig. 8.1 Results of Circulation Method (S=11mm)

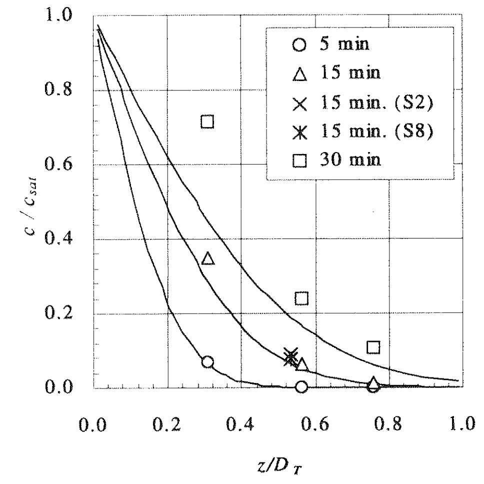

Fig. 8.2 Results of Circulation Method (S=6mm)

The symbol S2 and S8 in the legends indicate the sampling location in Fig. 4. The other data are sampled from S3, S4 and S5. Solid line is the result of calculation obtained from the method given in the section 5.1, one-dimensional molecular diffusion. Surface level was kept 11mm in Fig. 8.1 and 6mm in Fig. 8.2 respectively. Flow rate was about 12L/min for both cases.

following analysis. This assumption means that the concentration in the cargo tank varies with only vertical position and it is homogeneous in the horizontal plane. As shown in figure 8.1, the concentration at the sampling position S2 and S8 is almost same level, nevertheless the horizontal distance between these positions is the order of the tank length. Thus, this result indicates that one-dimensional diffusion advancing in the vertical direction is proper. It can be guessed that this fact results from the density of benzene gas that is about three times heavier than that of air. The solvent, air or nitrogen, including higher concentration of benzene gas becomes heavier and stratifies easily. Subsequently, it makes one dimensional concentration profile in the vertical direction.

Equation (1) shows the governing equation of one dimension molecular diffusion.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} \tag{1}$$

The origin of the coordinate system is located at the liquid surface. Therefore, the coordinate system moves upward with liquid surface during ordinary loading operation. The molecular diffusion coefficient is obtained by Chapman-Enskog theory [3, 4]. The boundary condition is assumed that the concentration at the liquid surface is the saturated concentration at the given atmospheric temperature as following,

$$c = c_{sat} \quad at \quad z = 0\ ,\ c = 0 \quad at \quad z = \infty \tag{2}$$

The saturated concentration is calculated by Antoine vapor pressure equation.[5]. The second boundary condition in equation (2) implies that there is no ceiling of cargo tank. The solution for the concentration of equation (1) under the boundary conditions represented by equation (2) is given by the following expressions [3].

$$c = c_{sat}\{1 - erf(\xi)\}\ ,\ \xi = \frac{z}{\sqrt{4Dt}} \tag{3}$$

where, the error function, *erf* is,

$$erf(\xi) = \frac{2}{\sqrt{\pi}}\int_0^{\xi} exp(-x^2)dx \tag{4}$$

The concentration of benzene gas emitted from cargo tank is defined to the concentration at the point of the tank top for the analysis of this model. Therefore, ullage space height, U in Figure 9, is substituted into z in the above equations for calculating concentration of the gas emitted from cargo tank. But, reference height is introduced for the estimation taking into account of the third diffusion mechanism described in section 3.2. The position of the estimation point for the emitted concentration is replaced with the reference height derived from the next section.

5.2 Advection under Tank Ceiling

Figure 7 in the paragraph 4.2.1, results of loading method, implies that advection under the tank ceiling should be considered. Figure 9 shows the schematic view to explain this diffusion mechanism associated with advection under tank ceiling.

In order to correct the difference between molecular diffusion and experimental data on the concentration of emitted benzene gas in Figure 7, reference height is introduced. The reference height is the height at where the concentration in cargo tank calculated by the molecular diffusion in the previous section coincides with the concentration detected in the vent pipe. The reference height is obtained from multiplying the ullage space height by coefficient, ζ as shown by equation (12). Figure 10.1 shows the relationship between ζ and surface height divided by the tank depth. The behavior of coefficient ζ was discussed as below.

The flow pattern formed in the gas space of the cargo tank should be dominated by Reynolds number based on the length of diagonal line in the horizontal cross section of the cargo tank, kinematic viscosity of the solvent gas and upward velocity of the surface of liquid benzene. Because there is no obstacle to characterize the flow pattern other than the variables described above. Reynolds number can be calculated by following equations,

$$Re = V_s L / \nu \tag{5}$$

$$L = \sqrt{L_T^2 + B_T^2} \quad , \quad V_s = Q_L/(B_T L_T) \tag{6}$$

In the case of nitrogen as solvent gas, the kinematic viscosity can be calculated by following equations,

$$\nu_s = \mu_s / \rho_s \tag{7}$$

$$\mu_s = 17.6 \times 10^{-6} \left\{ \frac{397}{T_a + 104} \right\} \left(\frac{T_a}{293} \right)^{3/2} \tag{8}$$

$$\rho_s = \frac{28.0}{22.4} \times \left(\frac{273}{T_a} \right) \tag{9}$$

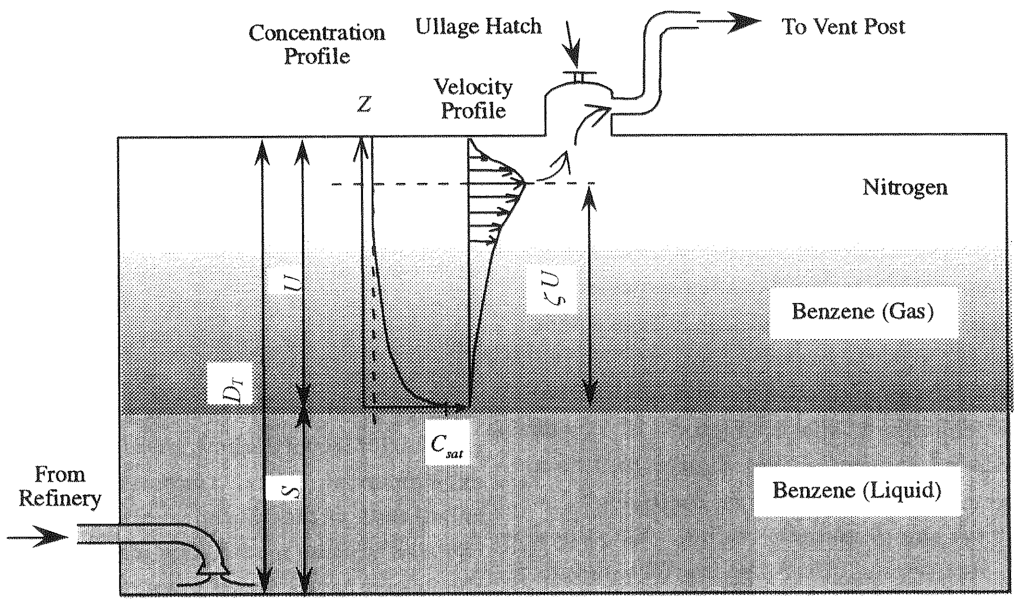

Fig. 9 Schematic View for the Diffusion in Cargo Tank

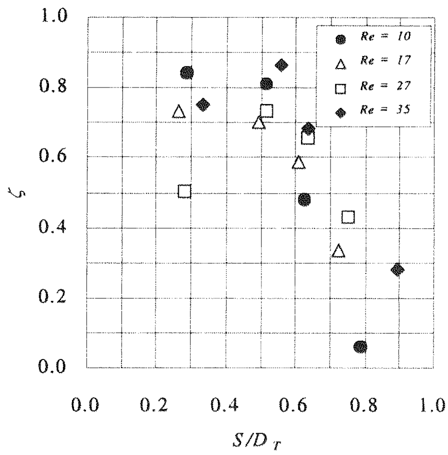

Fig. 10.1 Relationship Between Surface Height and Coefficient, ζ Obtained from Scale Model Experiment

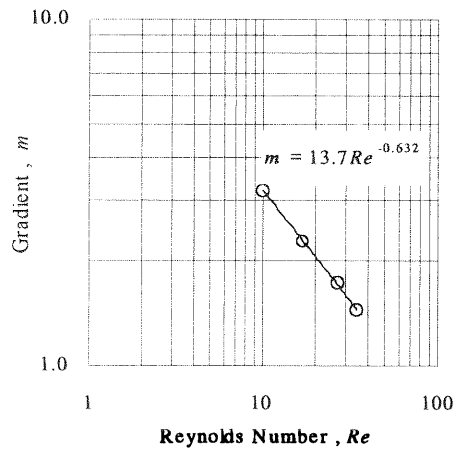

Fig. 11 The Relationship between Gradient, m and Reynolds Number

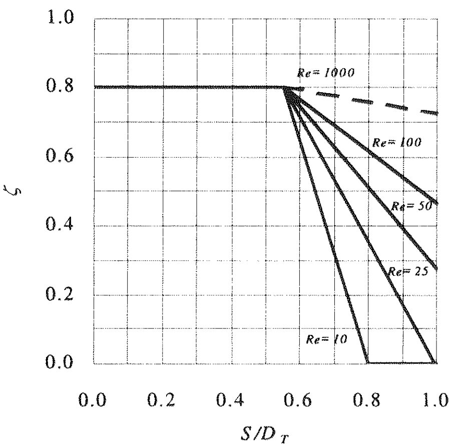

Fig. 10.2 Calculation Chart for Coefficient, ζ

Figure 10.1 also shows the Reynolds number doesn't affect to ζ when the liquid surface is low level. Furthermore, in initial period of loading operation, it can be guessed that ζ should be around unity and a constant value, because the surface is far from the tank ceiling and reference height is almost same to the distance between the liquid surface and the tank ceiling, ullage space height.

In terms of these quantitative and qualitative discussions described above, Figure 10.1 was summarized and converted into Figure 10.2 as a chart to calculate ζ. In this figure, coefficient ζ is correlated to the constant value, 0.8 when S/D_T<0.55. Meanwhile, after the surface height exceeds 55% of the tank depth, ζ decreases linearly and its slope is function of Reynolds number. This calculation chart for ζ in Figure 10.2, is written in the form of equations as following.

$$\begin{cases} \zeta = 0.8 \quad , \quad 0 \le S/D_T < 0.55 \\ \zeta = m(S/D_T - 0.55) + 0.8 \ , \ \ 0.55 \le S/D_T \le 1 \end{cases} \qquad (10)$$

Where, m is the gradient of the solid lines in Figure 10.2. The relationship between the gradient and Reynolds number is approximated by the following equation using experimental data shown in Figure 11.

$$m = -13.7Re^{-0.632} \qquad (11)$$

Finally, the reference height can be derived from following equation.

$$z_{ref} = \zeta U \qquad (12)$$

The ullage space height in Figure 9 is replaced with the reference height to estimate the concentration of emitted benzene gas.

The second diffusion mechanism associated with eddy diffusion above the liquid surface can be neglected for the scale model because of the shortness of its period. Figure 12 shows the comparison of result of calculation and experimental data indicated as Re=10 and 35. The calculation results show good agreement with the experimental data. However, these results calculated with reference height are limited in the size of scale model. The measurement data for the actual cargo tank shown in Figure 5 is plotted as Re=630 in Figure 12. The measurement value at S/D_T=0.74 is larger than the result of

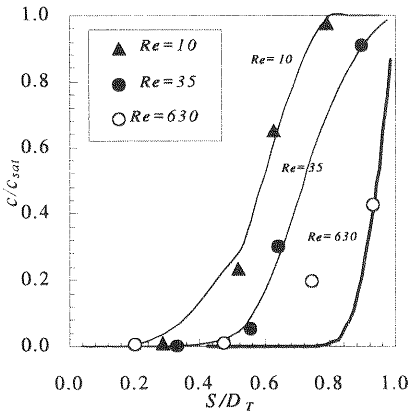

Fig.12 Comparison of the Experimental Data with Calculation Data Obtained from One-Dimensional Molecular Diffusion in the section 5.1 Combined with Reference Height in the section 5.2. : Plotted data represents experimental data and solid line is calculation

calculation with the Reynolds number based on the actual condition in Table 1. This discrepancy implies that another effect to make larger diffusion exists in the case of actual cargo tank size.

We considered that another effect to boost diffusion is the effect of eddy diffusion in the initial period of loading operation as described in paragraph 4.2.2. The method estimating the eddy diffusion coefficient is described in the next section.

5.3 Eddy Diffusion on Liquid Surface

Figure 8 in the paragraph 4.2.2, results of the circulation method, shows the effect of eddy diffusion on the liquid surface in the period that liquid surface is low. Instead of equation (1), diffusion equation taking account of the eddy diffusion can be expressed as equation (13) with assuming one-dimensional diffusion.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left\{D_{eff}\frac{\partial c}{\partial z}\right\} \tag{13}$$

Where, diffusion coefficient, D_{eff} is separated into molecular diffusion and eddy diffusion coefficient.

$$D_{eff} = D + D_t \tag{14}$$

The eddy diffusion coefficient, D_t depends on the flow condition of the gas phase. And it is function of time and space. The following paragraphs describe how to obtain its profile in the gas space of the cargo tank.

5.3.1 Eddy Viscosity in Liquid Phase

Firstly, the eddy viscosity profile of liquid benzene loaded into the cargo tank is derived.

Eddy viscosity is derived from the combination of length scale and velocity scale. To obtain velocity scale, transport equation of turbulence energy was used. Assuming that all energy supplied from the momentum energy of liquid benzene is exchanged to the turbulence energy, transport equation of turbulence energy yields as following expression with neglecting the pressure fluctuation [6].

$$\frac{\partial k_L}{\partial t} = \frac{\partial}{\partial z_L}\left\{\nu_{eff}\frac{\partial k_L}{\partial z_L}\right\} - \varepsilon \tag{15}$$

$$\nu_{eff} = \nu + \nu_t = \nu + l\sqrt{k_L} \tag{16}$$

Since there is no distinct length scale in the cargo tank, the length scale is determined to the diameter of loading pipe, l (m), in the cargo tank. Using this length scale, the equation for the dissipation rate, ε is derived by dimensional analysis with unknown quantity, c^*.

$$\varepsilon = c^* \frac{k_L^{3/2}}{l} \tag{17}$$

Substituting above dissipation rate into the equation (15),

$$\frac{\partial k_L}{\partial t} = \frac{\partial}{\partial z_L}\left\{\left(\nu + l\sqrt{k_L}\right)\frac{\partial k_L}{\partial z_L}\right\} - c^* \frac{k_L^{3/2}}{l} \tag{18}$$

Since upward surface speed is very small such as 1 (mm/s), the distribution of turbulence energy in the liquid phase can be considered as steady state condition at some surface level. By this assumption, equation (18) reduces to

$$\frac{\partial}{\partial z_L}\left\{\left(\nu + l\sqrt{k_L}\right)\frac{\partial k_L}{\partial z_L}\right\} = c^* \frac{k_L^{3/2}}{l} \tag{19}$$

Furthermore, using assumption that the molecular viscosity can be eliminated by the comparison between the molecular viscosity and the eddy viscosity,

$$\nu << \nu_t \left(= l\sqrt{k_L}\right) \tag{20}$$

Although this assumption doesn't reflect the precise physical condition, we can reduce the number of equation to be solved by the numerical analysis. Using above assumption, equation (21) yields

$$\frac{2l}{3}\frac{\partial^2 k_L^{3/2}}{\partial z_L^2} = c^* \frac{k_L^{3/2}}{l} \tag{21}$$

Integrating with respect to z_L, the profile of the turbulence energy, k_L is obtained by the below equation.

$$k_L = k_{0L}\exp\left(-\sqrt{\frac{2c^*}{3}}\frac{z_L}{l}\right) \tag{22}$$

The turbulence energy at the liquid surface, $k_L(z_L=s)$ can be calculated by the above equation with boundary condition. And following equation meaning the turbulence energy per unit area of tank bottom is used for this boundary condition at $z_L=0$.

$$k_{0L} = \frac{1}{2}(Q_L / A_P)^2 \frac{A_P}{B_T L_T} \tag{23}$$

5.3.2 Eddy Viscosity in Gas Phase and Diffusion Coefficient

In this paragraph, the eddy diffusion coefficient profile in the vertical direction of gas phase is derived. It is assumed that the movement of gas phase at the surface coincides with the movement of liquid phase for the boundary condition at the liquid surface. Therefore, the magnitude of turbulence energy of liquid and gas phase at the surface is same except for their density. Substituting the surface level, S into z_L in the equation (22), the turbulence energy of liquid phase at the surface is obtained.

$$k_{0G} = k_{0L}\exp\left(-\sqrt{\frac{2c^*}{3}}\frac{S}{l}\right) \tag{24}$$

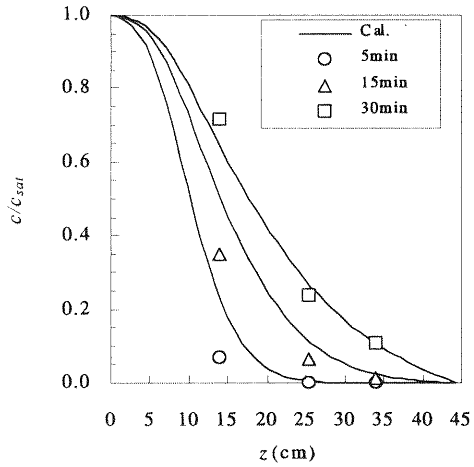

Fig.13.1 c^* =10

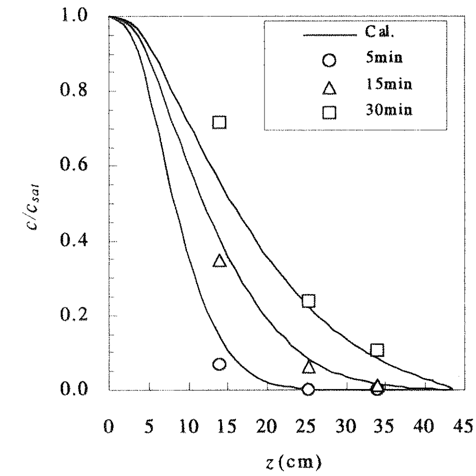

Fig.13.2 c^* =25

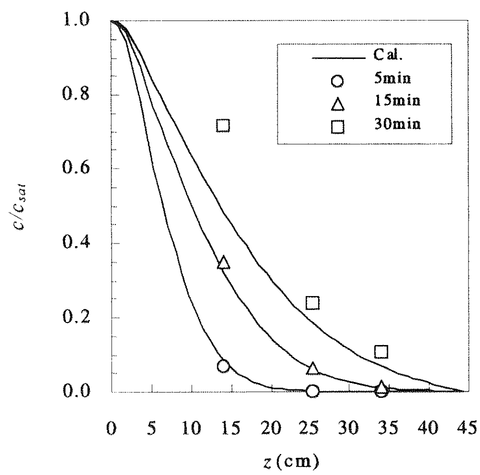

Fig.13.3 c^* =100

Fig.13 Time History of Concentration Profile: Symbols are experimental data when surface level, S, is 6 (mm) and solid lines are calculation.

Using this value as boundary condition at the surface of liquid benzene, turbulence energy in the gas phase is derived as following equation that is same to equation (22).

$$k_G = k_{0G}\exp\left(-\sqrt{\frac{2c^*}{3}}\frac{z}{l}\right) \quad (25)$$

Assuming Reynolds Analogy, the eddy diffusion coefficient can be calculated with equation (26).

$$D_t = l\sqrt{k_G} \quad (26)$$

Finally, the eddy diffusion coefficient becomes function of turbulent energy that depends on the time and space by above equation. The concentration profile is calculated with equations (13), (14), (22), (23), (24) and (25).

In the case of that the diffusion coefficient in the equation (13) depends on z, we must use the numerical method to obtain time history of the concentration profile [7].

5.3.3 Parametric Analysis

The unknown quantity, c^* must be determined to estimate the distribution of eddy viscosity in the vertical direction. To obtain appropriate value, parametric analysis to find out the value of c^* was carried out for both surface levels, S=6(mm) and S =11(mm) in Figure 8. Figure 13 and 14 represent the results of parametric analysis with experiment data shown in Figure 8.1 and 8.2. In these figures, the solid lines indicate result of calculation with changing the value of c^*. From these figures, calculated line with c^*=25 seems to give a proper results for both surface levels.

Figure 15 represents the profile of diffusion coefficient including both the eddy diffusion and the molecular diffusion calculated with c^*=25. In this figure, the liquid surface level was fixed at 6(mm) and 11(mm) by circulating liquid benzene in the model cargo tank and the flow rate was 12 (L/min) for both cases. The diffusion coefficient above the surface is about one order of magnitude larger than that of molecular diffusion coefficient. The diffusion coefficient decreases sharply and reaches to the order of molecular diffusion within several centimeters from the surface.

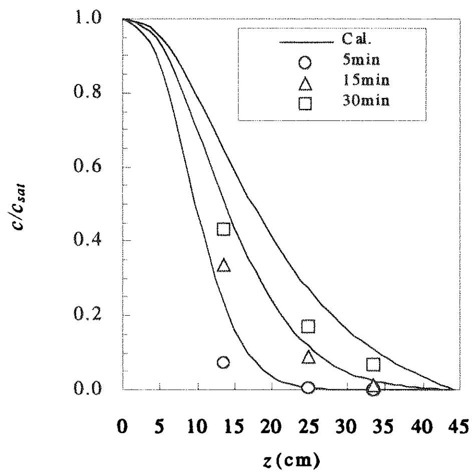

Fig.14.1 c^* =10

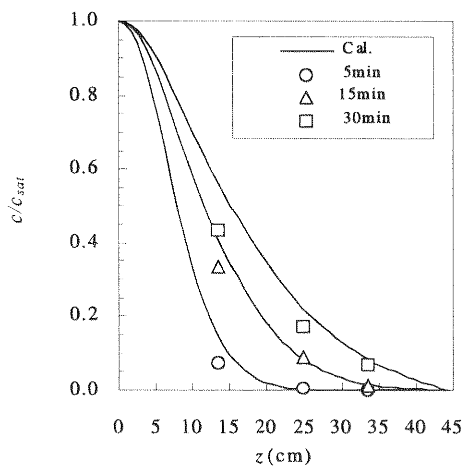

Fig.14.2 c^* =25

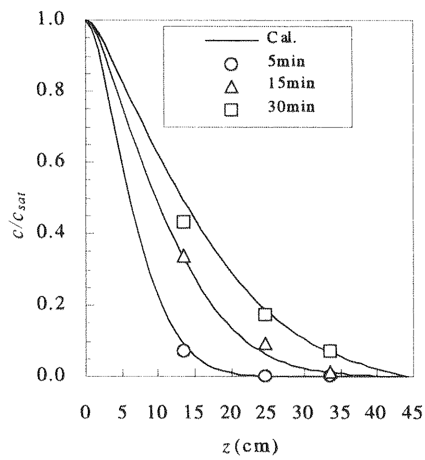

Fig.14.3 c^* =100

Fig.14 Time History of Concentration Profile: Symbols are experimental data when the surface level, S, is 11 (mm) and solid lines are calculation

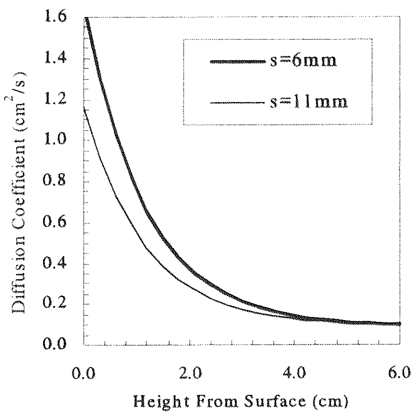

Fig.15 Distribution of Diffusion Coefficient in the Scale Model Tank during Circulation Method

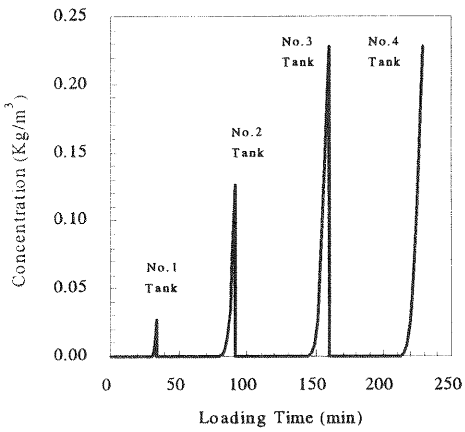

Fig.17 Time History of Concentration for All Tanks on Chemical Tanker

Both methods given in the section 5.2 on the reference height and section 5.3 on the eddy diffusion are combined to calculate the concentration of emitted benzene gas from cargo tank during benzene loading operation.

6. Result and Discussion

To investigate the calculation model built in the previous chapter, result of calculation was compared with the experimental data obtained with the scale model and the prototype. Figure 16 shows this comparison in the same manner as that of figure 12. In the case of the experimental data with the scale model indicated by black circle and triangle symbols, benzene diffuses in the tank under the domination of molecular diffusion and the calculation results in good agreement. Meanwhile, the calculation result for prototype indicated by thicker solid line agrees approximately with experimental data, nevertheless the simplification in the procedure to build up the calculation model in the previous chapter, it can be considered that this calculation model is useful in terms of order estimation.

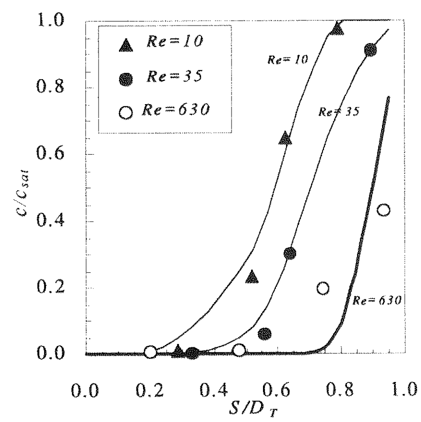

Fig.16 Comparison of the Experimental Data with Calculation Data obtained from final calculation model considering three factors in section 3.2 : Plotted data represents experimental data and solid line is calculation

Figure 17 shows the result of calculation applied to the all tanks placed on a 499GT chemical tanker. The data set for tank dimensions of these cargo tanks and loading condition are summarized in Table 2. These values are referred to an actual condition of benzene loading operation. Total volume and mass of liquid benzene loaded into the cargo tanks are 1142 (KL) and 1000 (ton) respectively. It takes about 230 minutes to complete the whole loading operation. Since the order of loading operation is same to the Tank No., time history of the concentration represents four peaks corresponding to each cargo tank. But, the concentration peak for No.1 cargo tank is stopped at lower level than that of the other tanks. This phenomenon is caused from the loading rate set to 85% that is lower than the other tanks. Thus, the layer including high concentration benzene gas doesn't reach to the tank ceiling and it doesn't

Table 2 Typical Tank Dimension and Loading Condition of 499GT Chemical Tanker

Tank No.	No.1	No.2	No.3	No.4
Length	5.0 m	8.0 m	9.0 m	9.0 m
Breadth	4.0 m	4.0 m	4.0 m	4.0 m
Depth	5.0 m	5.0 m	5.0 m	5.0 m
Volume (P+S)	200 m^3	320 m^3	360 m^3	360 m^3
Loading Rate	85 %	90 %	95 %	95 %
Flow Rate	300 KL/hr			
Liq. Benzene Temperature	20 Celsius Degree (293 Kelvin)			
Air Temperature	20 Celsius Degree (293 Kelvin)			
Diameter of Loading Pipe	0.15 m			

supply high concentration benzene gas into the vent line connected to the ullage dome located at the tank ceiling. Total emission is estimated as about 16 (kg) and emission factor [8] defined to the quantity of emission into the atmosphere divided by the quantity of loaded substances is calculated as 0.014 (kg/kL).

7. Conclusions

A new calculation method was successfully developed to estimate the concentration of benzene gas emitted from cargo tank during benzene loading operation. Further more, this model which includes three diffusion mechanisms in the cargo tank as followings is simple so that a spread sheet software、such as Excel, can be applied.

1. While the liquid surface level is low enough to agitate the gas phase above the surface, the concentration flux above the surface is larger than that of molecular diffusion owing to the eddy diffusion. But this period is too short to affect the concentration profile for the size of the scale model of cargo tank. On the other hand, this effect should be estimated for the size of the actual cargo tanks placed on the chemical tankers.
2. The concentration profile in the scale model of cargo tank during ordinary loading operation is almost one-dimensional in the vertical direction except in the vicinity of the tank ceiling.
3. When the surface of liquid benzene closes to the tank ceiling, concentration estimated with one-dimensional molecular diffusion differs from experimental data because of the advection, and this difference can be corrected by introducing reference height that is function of the ratio of ullage height to the tank depth and Reynolds number.

Nomenclature

A_p=area of cross section of loading pipe, m^2
B_T = tank breadth, m
c=concentration of benzene gas, ppm
c_{sat}=saturated concentration of benzene, ppm
c^*=coefficient for dissipation rate
D= molecular diffusion coefficient of benzene gas, m^2/s
D_t=eddy diffusion coefficient, m^2/s
D_T= tank depth, m
k_L= turbulence energy of liquid phase, m^2/s^2
k_G= turbulence energy of gas phase, m^2/s^2
l=diameter of loading pipe, m
L= representative length for Reynolds number, m
L_T = tank length, m
Q_L= loading flowrate, m^3/s
Re= Reynolds number
S= surface level of liquid benzene, m
T_a= temperature, K
t= time, sec
U= ullage space height, m
V_S= upward velocity of surface, m/s
z= vertical axis which origin is at surface, m
z_L= coordinate system in the vertical direction which origin is fixed at tank bottom, m
z_{ref}= reference height, m
ε= dissipation rate, m^2/s^3
μ_s= viscosity of solvent gas, Pa sec
ν_s= kinematic viscosity of solvent gas, m^2/s
ν= kinematic viscosity of liquid benzene, m^2/s
ν_t= eddy viscosity of liquid benzene, m^2/s
ρ_s= density of solvent gas, kg/m^3
ζ= coefficient for reference height

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