CHAPTER IV

RESULTS AND DISCUSSION

4.1 An Investigation of Factors Affecting the Efficiency of the Progressive Freeze-concentration in the Ionic Solutions

4.1.1 Effects of the Stirring Speed at the Ice Front (N_r) and the Advance Rate of the Ice Front (u)

The effective partition coefficients (K) of the ionic solutions can be calculated following Eq. (2.4). The sample of calculation of the K value is shown in Appendix A. The effect of stirring speed at the ice front on the effective partition coefficients (K) of the ionic solutions; LiCl, NaCl, KCl, and CsCl, with the initial concentrations of 2.5 % (w/w) were shown in Figure 4.1. It was found that the effective partition coefficient, K, decreased with an increase in stirring speed. This finding indicates that an increase in stirring speed at the ice front enhances the performance of the freeze-concentration, especially in LiCl, NaCl, and KCl solutions.

This is because an increase in stirring speed enhances the rate of mass transfer of both cations and anions from the ice-solution interface into the bulk solution; thus lowering the chance that cations and anions are trapped in the ice layer.
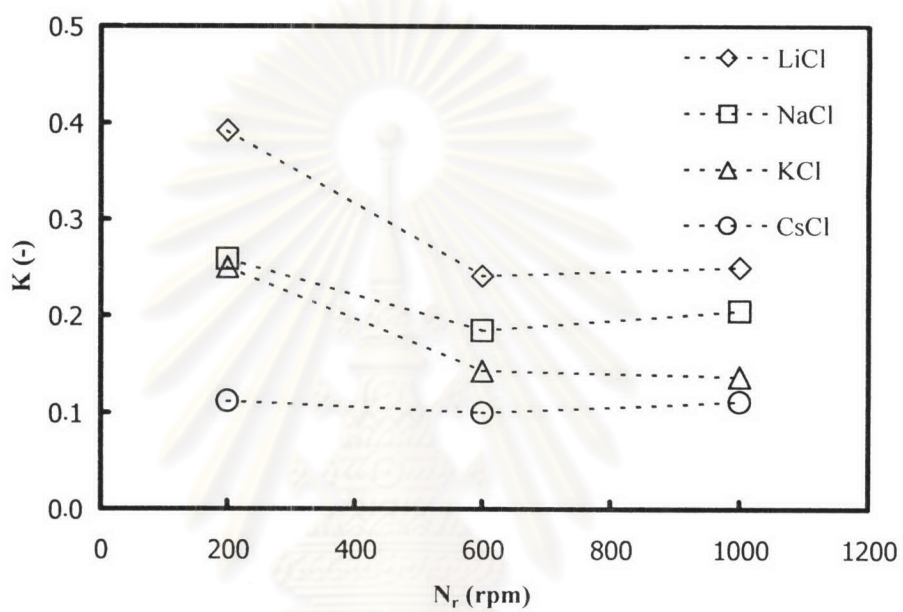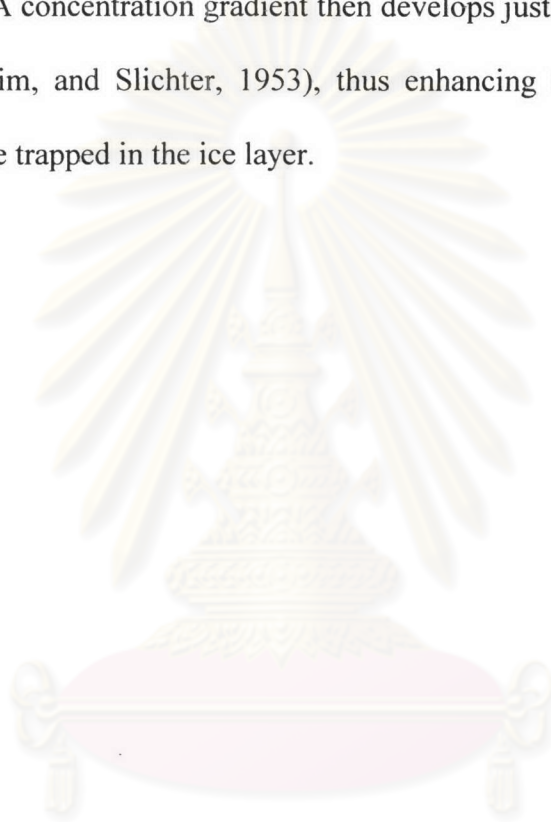
Fig. 4.1 Effect of the stirring speed (N_r) on the effective partition

coefficients (K) of the 2.5 % (w/w) LiCl, NaCl, KCl, and CsCl

solutions

Since K essentially decreases with an increase in mass transfer coefficient (k) as illustrated in Eq. (2.13), an increase in k leads to a decrease in K, or *vice versa*. In addition, the level off of the K value at a specific point is due to the fact that N_r has a power of 0.2. The change in N_r at a lower range is more significant to the K value than that at a higher range. This agrees well with Halde (1979), Lui *et al.* (1997), and Chen *et al.* (1998).

The advance rate of the ice front (u) in this experiment was calculated following Eq. (3.1). The sample of calculation of the advanced rate of the ice front is shown in Appendix C. The effect of this parameter on the effective partition coefficients of the 2.5% (w/w) LiCl, NaCl, KCl, and CsCl solutions at a stirring rate of 600 rpm is shown in Figure 4.2. It was found that an increase in an advance rate of the ice front resulted in a sharp increase in the K value. This indicates that the advance rate of the ice front strongly affects the concentration change during the progressive freeze-concentration. It was also found that, at the same advance rate, the K values of these 4 types of the ionic solutions were different. The order of the K values was as follows: LiCl > NaCl > KCl > CsCl. The order of the diffusion coefficients of the cations of these molecules, however, was in the other way round (Cussler, 1997). This is probably due to the fact that, when an ionic molecule is dissolved in water; it does not diffuse in water as a single molecule; it is, on the contrary, dissociated into a cation and an anion, and these ions are able to move freely in the solution. Since all solutions contain the same anion (*i.e.* Cl⁻), the diffusion properties of these ionic solutions are dictated by cations. Because of its low ability to diffuse from the moving ice-liquid interface to the bulk solution, LiCl is easily trapped within the ice layer. Consequently, LiCl whose diffusivity is lower than that

of NaCl, KCl, and CsCl, respectively, possesses the highest K value or, in other words the highest inclusion in the ice phase (Cussler, 1997).

Moreover, an increase in the advance rate of ice front results in an increase in the amount of solute rejected from the ice layer. The solute rejected from the ice layer then accumulates at the interface between the ice layer and the bulk solution. A concentration gradient then develops just ahead of the advancing crystal (Burton, Prim, and Slichter, 1953), thus enhancing the possibility that the solute molecules are trapped in the ice layer.
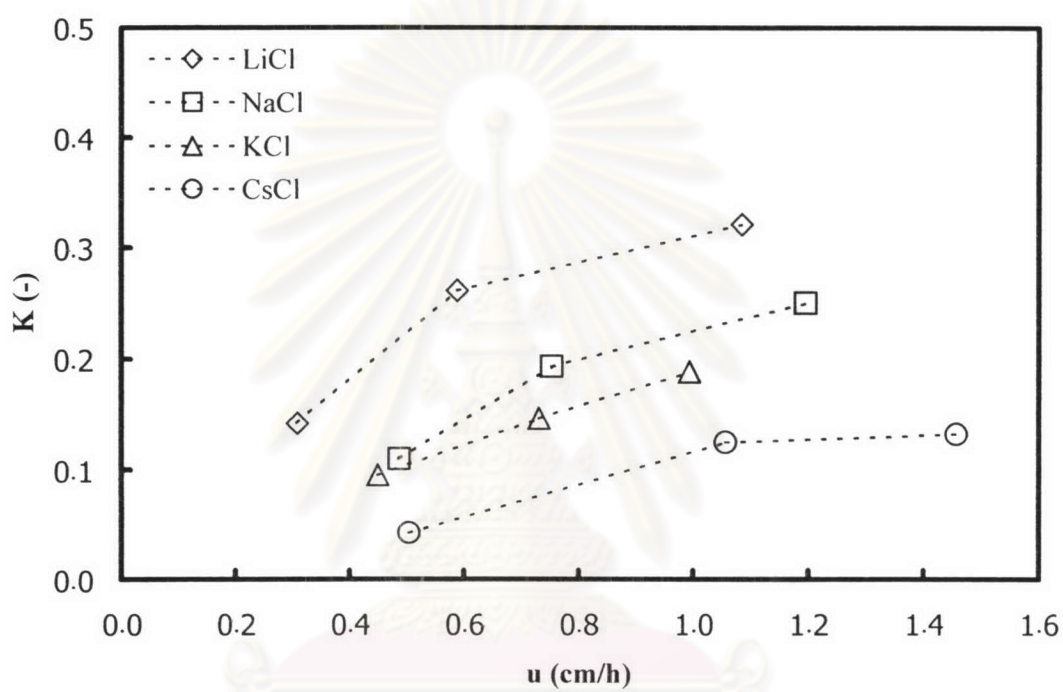
Fig. 4.2 Effect of the advance rate of the ice front (u) on the effective partition coefficients (K) of the 2.5%(w/w) LiCl, NaCl, KCl, and CsCl solutions at a stirring speed of 600 rpm

4.1.2 Effects of the Operating Conditions and the Initial Concentration (C_0) of the Ionic Solution on the Effective Partition Coefficient (K)

According to Eq. (2.16), it is clear that the relationship between the K value and the operating conditions is not linear, as shown in Figure 4.3, thus making it difficult to determine the limiting partition coefficient (K_0) and the a constant. In order to overcome this problem, Eq. (2.16) is then rewritten or linearized as follows:

$$\ln [(1/K) - 1] = \ln [(1/K_0) - 1] - (1/a)[u/N_r^{0.2}] \qquad (4.1)$$

A plot between $\ln [(1/K) - 1]$ and $u/N_r^{0.2}$ gives a linear line with a slope of $-1/a$ and a y-intercept of $\ln [(1/K_0) - 1]$. It was found, from Figure 4.4, that the model (Eq. (4.1)) is adequately fitted with the experimental data; $R^2 = 0.7873$, 0.8056, 0.8933, and 0.8256 for the CsCl, KCl, NaCl, and LiCl solutions, respectively.
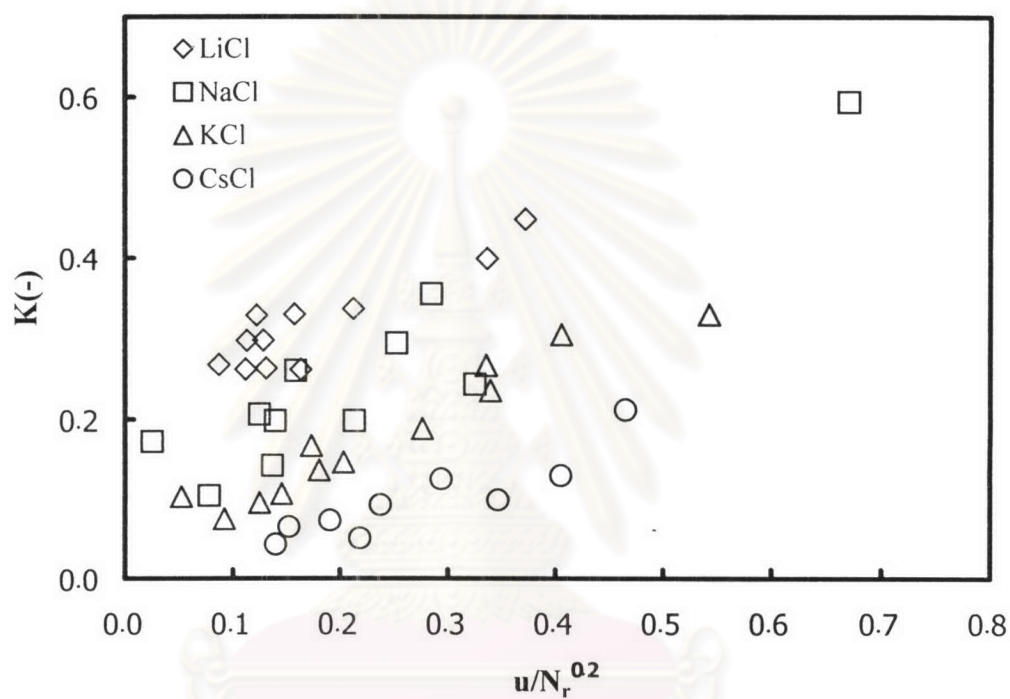
Fig. 4.3 Effects of the operating conditions on the effective partition coefficient of ionic solution at 2.5 %(w/w).
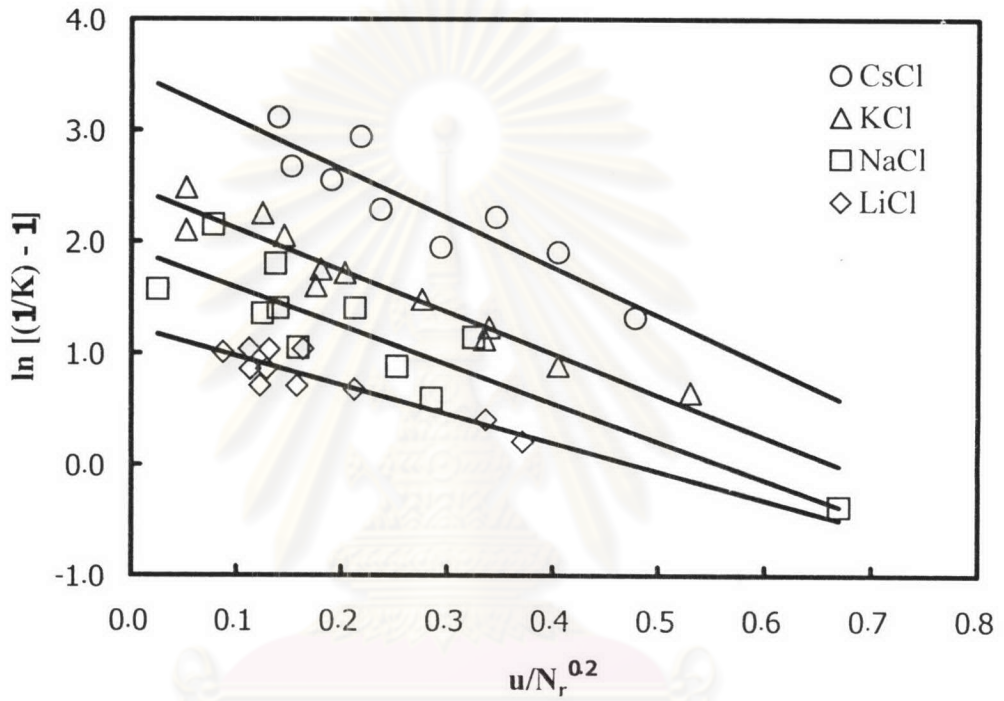
Fig. 4.4 Effects of the advance rate of the ice front (u) and the stirring speed

(N$_r$) on the effective partition coefficient (K) of the 2.5%(w/w) CsCl,

KCl, NaCl, and LiCl solutions

The effect of the initial concentration of the LiCl solution on the K value is illustrated in Figure 4.5. It was found that the solute concentration is proportional to the K value. The lower the LiCl initial concentration, the lower the K value, thus resulting the better performance of the freeze-concentration.

Similar plots between $u/N_r^{0.2}$ and $\ln [(1/K) -1]$ of NaCl, KCl, and CsCl solutions are shown in Figures 4.6, 4.7, and 4.8, respectively. It was found that a decrease in the advance rate of the ice front (u) and an increase in the stirring speed (N_r) caused the K value to decrease. It was also found that an increase in the initial concentration of a solution resulted in an increase in the K value, thus leading to a decrease in the value of $\ln [(1/K)-1]$. This confirms that the initial concentration of a solution has a significant effect on the efficiency of this process. This is in good agreement with Halde (1979), who suggested that the progressive freezing of the NaCl solution with a high initial concentration was more difficult to purify than that with the lower ones, due to the depression of the freezing point.
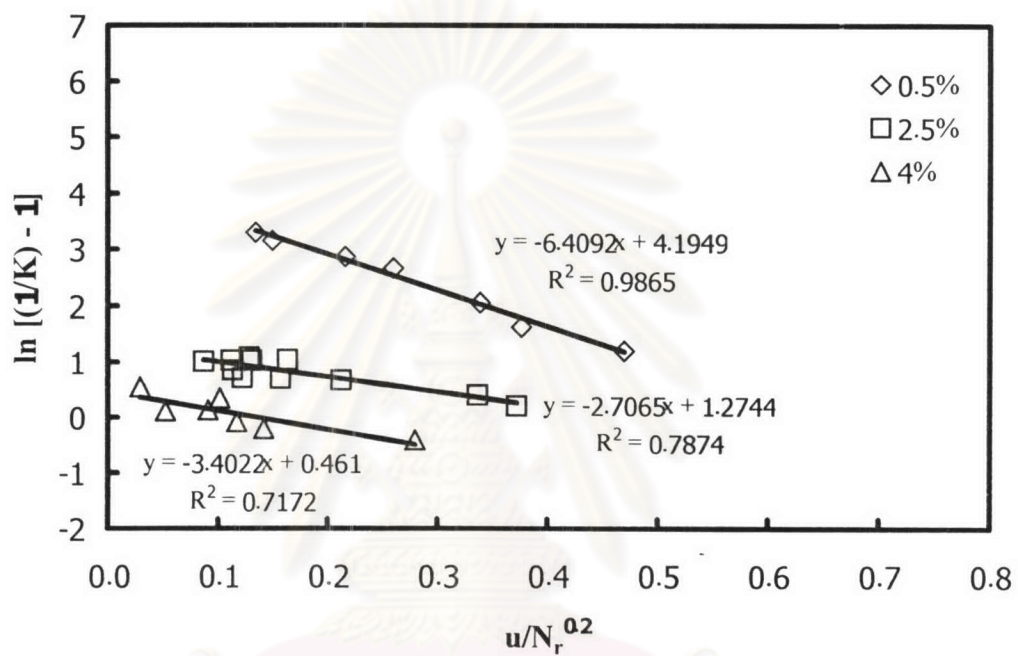
Fig. 4.5 Effects of the initial concentration (C_0) of LiCl solution and the operating conditions on the effective partition coefficient (K)
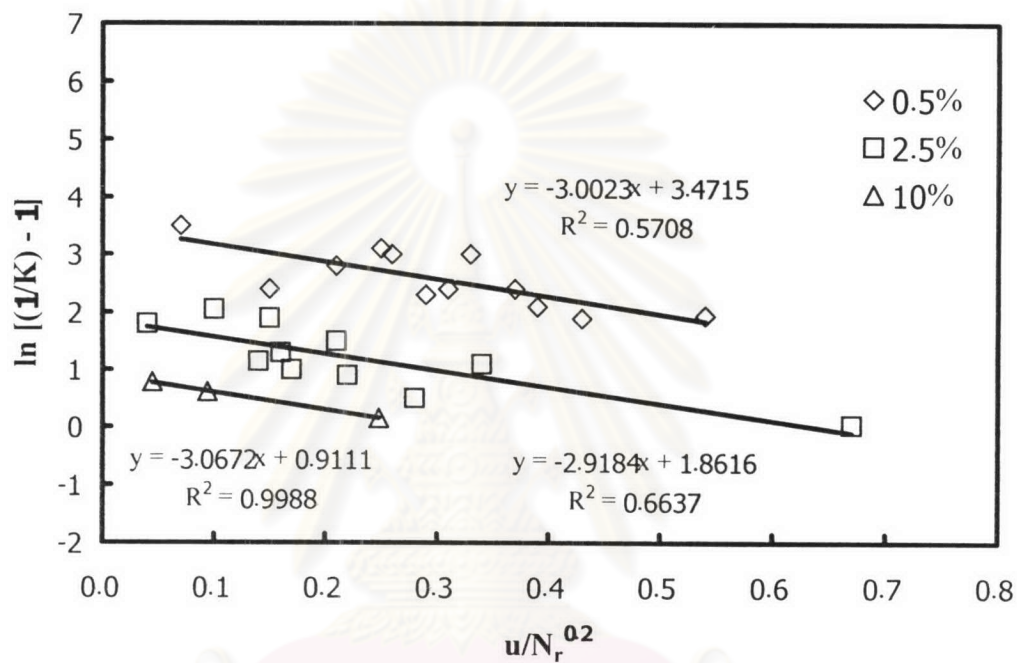
Fig. 4.6 Effects of the initial concentration (C_0) of NaCl solution and the operating conditions on the effective partition coefficient (K)
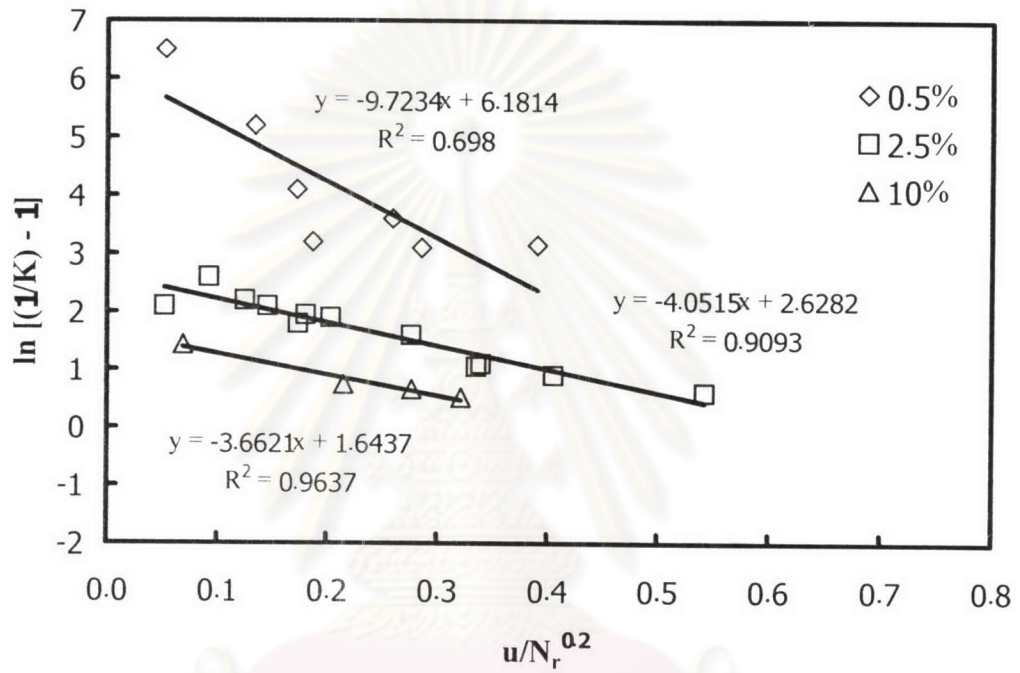
Fig. 4.7 Effects of the initial concentration (C_0) of KCl solution and the operating conditions on the effective partition coefficient (K)
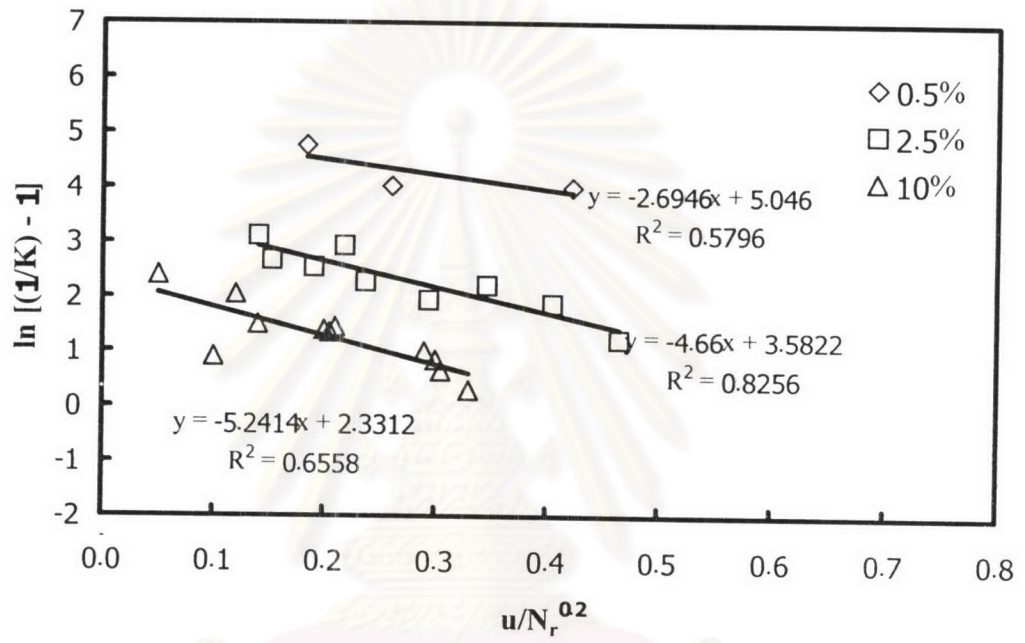
Fig. 4.8 Effects of the initial concentration (C_0) of CsCl solution and the operating conditions on the effective partition coefficient (K)

4.1.3 Determination of the Limiting Partition Coefficient (K_0) of an Ionic Solute Based on the Concentration Polarization Model

From Figures 4.5–4.8, the limiting partition coefficient, K_0, can be obtained by extrapolating each line to the point where $u/N_r^{0.2}$ is equal to zero (*i.e.* a y-intercept of each line). At the point where $u/N_r^{0.2}$ is equal to zero, K_0 is independent of the operating conditions. Hence, K_0 depends directly on the type and concentration of a solute. In other words, K_0 is one of the important characteristic properties of the progressive freeze-concentration.

The relationship between the partition coefficient (K_0) and the initial concentration (C_0) ranging from 0.5–10 % (w/w) of LiCl, NaCl, KCl, and CsCl is shown in Figure 4.9. It was found that K_0 of all ionic solutions (*i.e.* salts) depend linearly on their initial concentrations. An increase in the initial concentration caused K_0 to increase.

In order to verify that the dependence of K_0 on C_0 (*i.e.* a slope of a plot between C_0 and K_0) is related to the structure of a solute, the slope of a C_0-K_0 plot of each solute is plotted against the hydration number, obtained from Cussler (1997), of a cation of each solute, as shown in Figure 4.10.

It was found, from Figure 4.10, that the relationship is linear with R^2 of 0.9895. This is due to the fact that ions are dissolved in water; they either lower or enhance the ice-like structure. If the ions enhance the structure, these ions are immediately surrounded by water that is more organized than water in the bulk solution, thus resulting in a higher viscosity. Accordingly, such ions diffuse more slowly than expected. On the other hand, if the ions destroy the structure, they are immediately surrounded by water of a reduced viscosity. These ions then diffuse more quickly than expected. The ions of Li^+ and Na^+ are in the former group.

Additionally, they have strong electric fields and are net structure formers. The diffusivities of these ions are, therefore, low, thus resulting in the higher K values than those of K^+ and Cs^+ ions, which are in the latter group (*i.e.* the ions that destroy the ice-like structure when dissolved) (Cussler, 1997). In additional, Cussler (1997) reported that the hydration numbers of Li^+, Na^+, K^+, and Cs^+ is 2.8, 1.2, 0.9, and 0.5 respectively. These hydration numbers are the same order as the K value in this study. Therefore, it could be concluded that the K value was proportional to the hydration properties of solute.
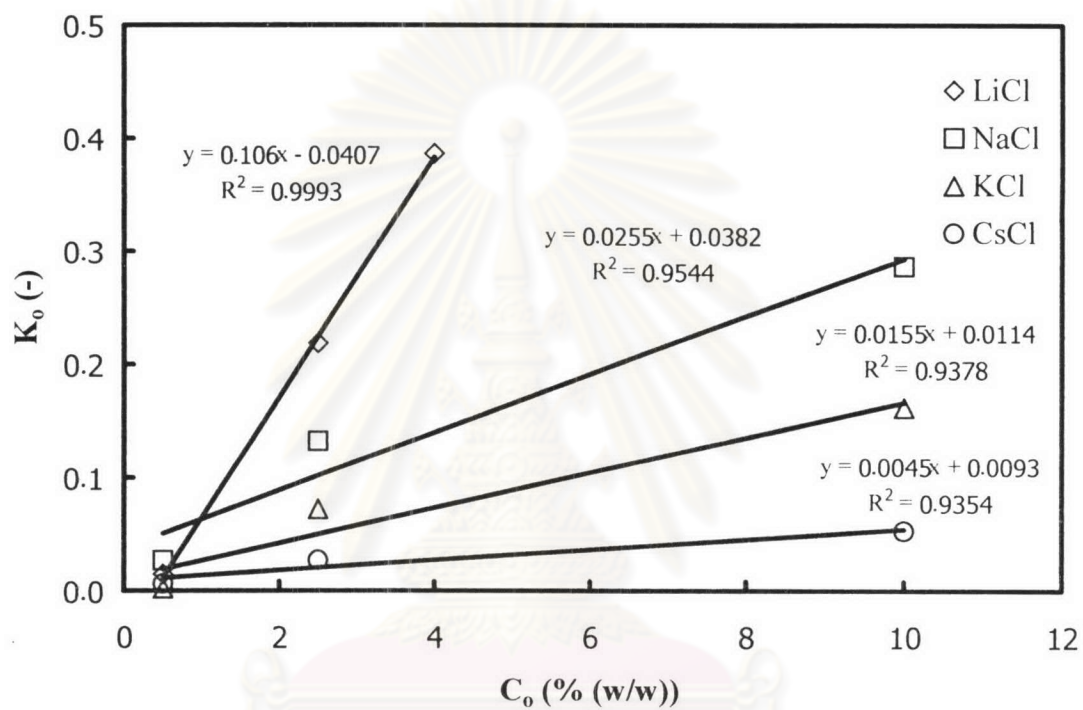
Fig. 4.9 Effects of type of salt and its initial concentration (C_0) on the limiting
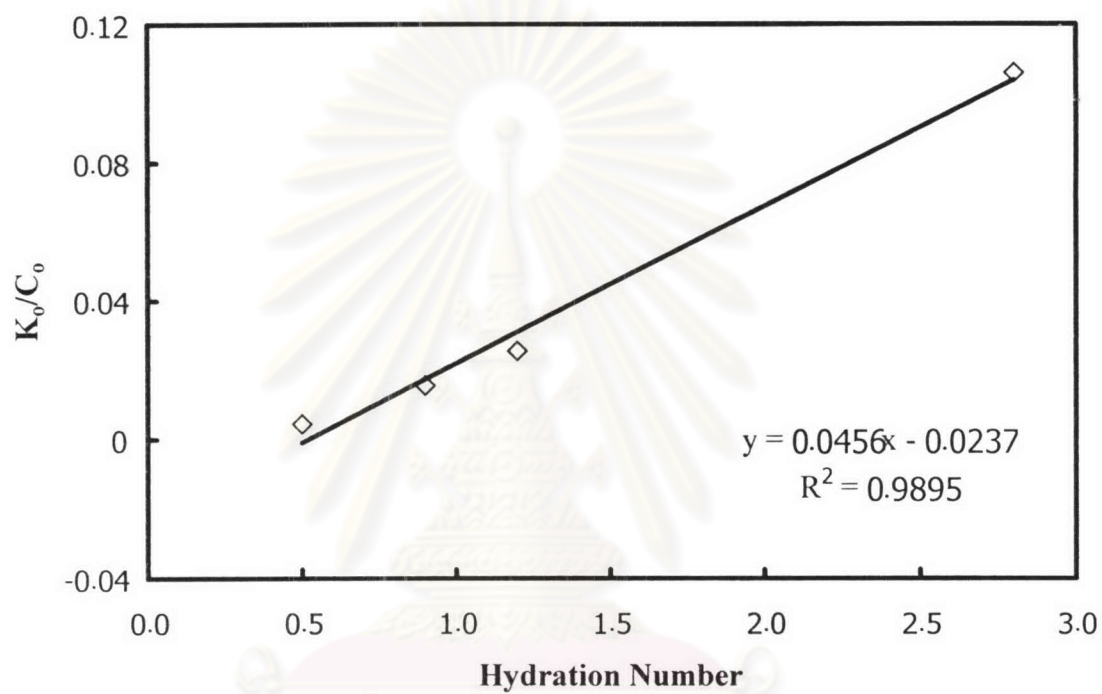
partition coefficient (K_0)

Fig. 4.10 The relationship between the hydration number and the K_0/C_0

Since C_{Li}, which is used to define K_0, is the value at the condition where $u/N_r^{0.2}$ is approaching zero. At this condition, it can be expected that the concentration profile in the bulk solution does not exist. Hence, C_{Li}, the concentration of a solute in the liquid just adjacent to the ice-liquid interface, is then equal to C_L, the concentration of a solute in the bulk solution. Consequently, C_S can be obtained when K_0 and C_L are obtained following Eq. (2.12).

A plot between C_S and C_L at equilibrium (*i.e.* a phase equilibrium plot) is illustrated in Figure 4.11. This plot illustrates that an increase in the amount of impurity, resulting from an increase in the concentration of a solute in the bulk solution, depends strongly on the type of solute.
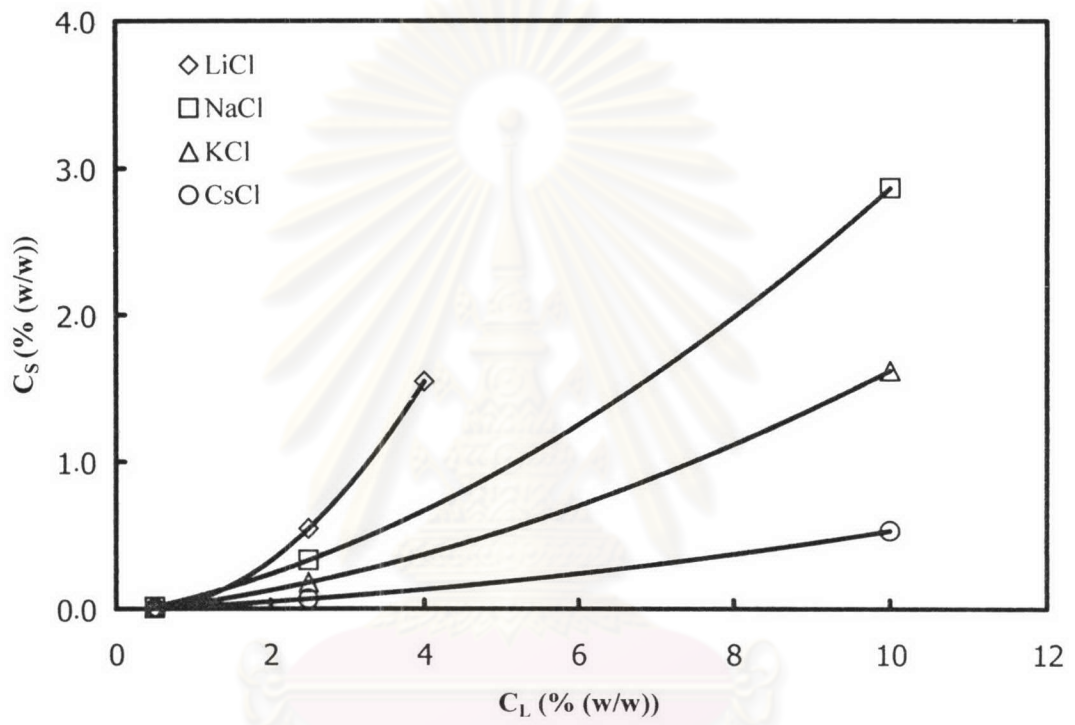
Fig. 4.11 A phase equilibrium plot of the LiCl, NaCl, KCl, and CsCl solutions

4.2 **An Investigation of Factors Affecting the Efficiency of the Progressive Freeze-concentration in the Non-ionic Solutions**

4.2.1 <u>Effects of the Stirring Speed at the Ice Front (N_r) and the Advance Rate of the Ice Front (u)</u>

The effect of the stirring speed at the ice front on the effective partition coefficient of the non-ionic solutions, D-(−)-ribose, D-(+)-glucose, D-(−)-fructose, lactose, and sucrose, at initial concentration of 10.0% (w/w) is shown in Figure 4.   . It was found that an increase in the stirring speed resulted in a decrease in the effective partition coefficient (K). Moreover, it was found that the K values of all non-ionic solutions were not affected by the type of solute (*i.e.* sugar). These indicate that the effective partition coefficient, K, was strongly dependent on the stirring speed at the ice front, but independent of the type of solute. It is noteworthy that the effect of the stirring speed on the K values of the non-ionic solutions is similar to that of the ionic ones.

The effect of the advance rate of the ice front on the effective partition coefficients of 10.0% (w/w) the non- ionic solution, comprising D-(−)-ribose, D-(+)-glucose, D-(−)-fructose, lactose, and sucrose, at a stirring speed of 600 rpm is shown in Figure 4.13.

It was found that the K value of the progressive freeze-concentration of the D-(−)-ribose, D-(+)-glucose, D-(−)-fructose, and sucrose solutions slightly increased with the advance rate of the ice front.
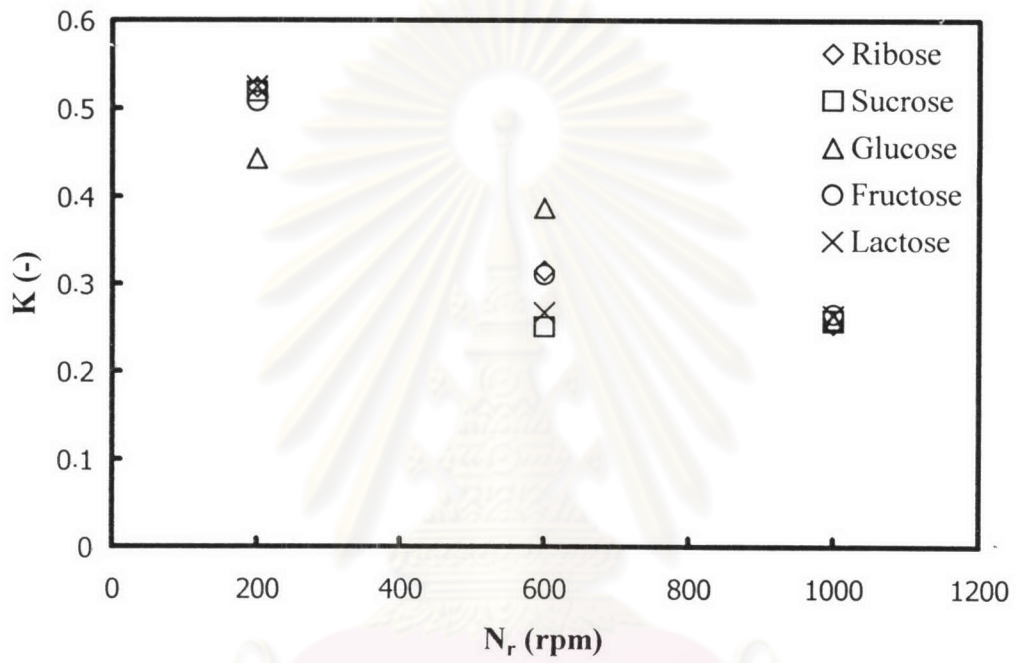
Fig. 4.12 Effect of the stirring speed (N_r) on the effective partition coefficients
(K) of the 10.0% (w/w) D-(–)-ribose, D-(+)-glucose, D-(–)-fructose,
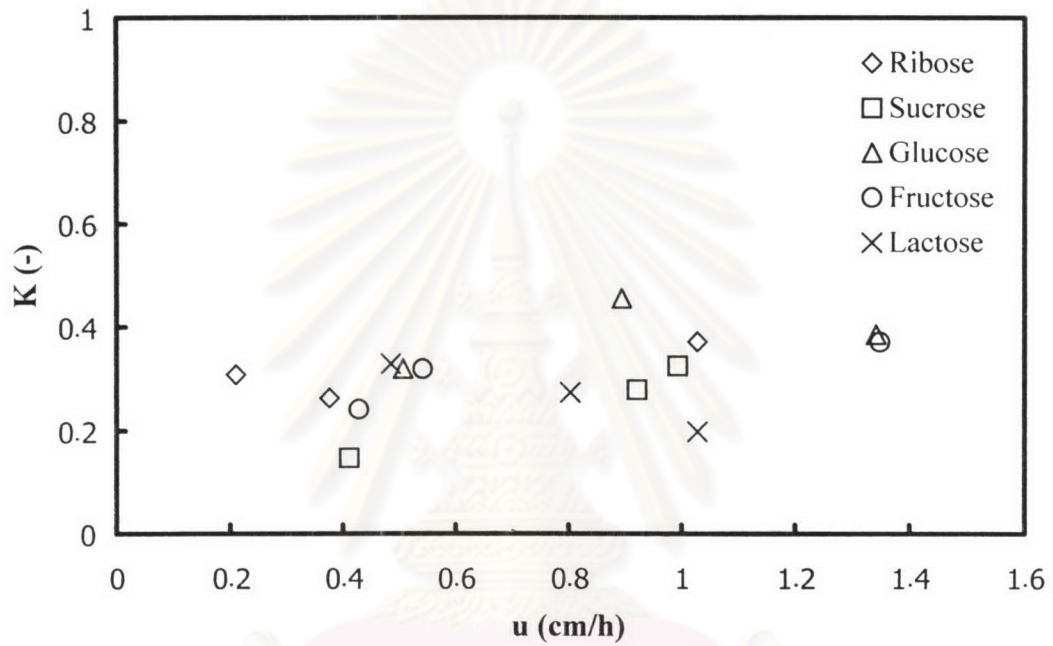lactose, and sucrose solutions

Fig. 4.13 Effect of the advance rate of the ice front (u) on the effective partition coefficients (K) of 10.0% (w/w) D-(-)-ribose, D-(+)-glucose, D-(-)-fructose, lactose, and sucrose solutions at a stirring speed 600 rpm

When considering the effects of stirring speed (N_r) and advance rate of ice front (u) on the K value of each non ionic solution, it was found that, at the same initial concentration, the K values of all types of sugars are insignificantly affected by the operating conditions, as illustrated Figures 4.14. This is because the interaction between water and non-ionic substance is weaker than that of the water-ionic substance, and about the same strength as that of water-water hydrogen bond (Fennema, 1996).

A solute capable of H-bond might be expected to enhance or, at least, not disrupt the normal structure of pure water (Fennema, 1996). Thus, non-ionic solutes were rejected from the ice layer. Consequently, the concentration profile at the interface was formed. When the system was stirred (*i.e.* N_r was increased), it enhanced diffusivities of molecules. In parallel, a lower advance rate of the ice front resulted in a lower possibility that molecules were trapped in the ice layer, thus enhancing the diffusion rate of molecules from the ice layer into the bulk solution. This resulted in a decrease in the K values.

4.2.2 Effects of the Operating Conditions and the Initial concentration (C_0) of the Non-ionic Solutions on the Effective Partition Coefficient (K)

Since the concentration polarization model could also be applied to the non-ionic solutions (i.e. sugars in this research), a similar analysis could also be extended for the non-ionic solutions, as shown in Figures 4.14 - 4.17.

It was found, from the figures, that a decrease in the advance rate of the ice front (u) and an increase in the stirring speed (N_r) resulted in a

sharp increase ln $[(1/K) -1]$ or a decrease in the K value. It should be noted, however, that the type of solute (or sugar) did not affect the K value.

The effects of the operating conditions and the initial concentration of the non-ionic solutions on the K value during the progressive freeze-concentration are shown in Figure 4.18. It was found that, when the solute concentration decreased, it caused the effective partition coefficient to decrease, indicating a better freeze concentration ratio. This result agrees with that of the ionic solution.

The possible explanation to this phenomenon might be that a decrease in solute concentration results in an increase in the mass transfer coefficient, thus enhancing the transportation of molecules of solutes from the ice layer into the bulk solution (Chen *et al.*, 1998). Additionally, Halde (1979) stated that, when the concentration of a dissolved substance is high, the solute remains even more concentrated near the ice-liquid interface, thus resulting in a depression of the freezing point of the liquid. The temperature then falls below the freezing point of the rest of the solution, and a subsequent increase in of the constitutional supercooling causes freezing at some distance from the ice-liquid interface, trapping the layer high in solute.
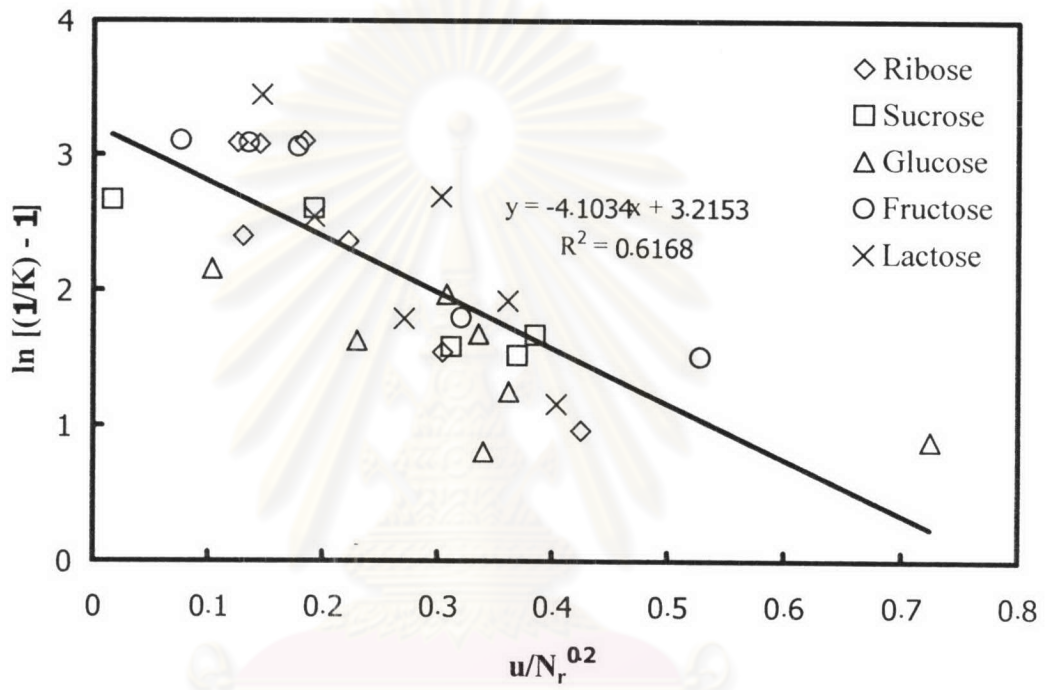
Fig. 4.14 Effects of the advance rate of ice front (u) and the stirring speed (N_r) on effective partition coefficient (K) of the non-ionic solutions at the concentration of 2.5% (w/w)
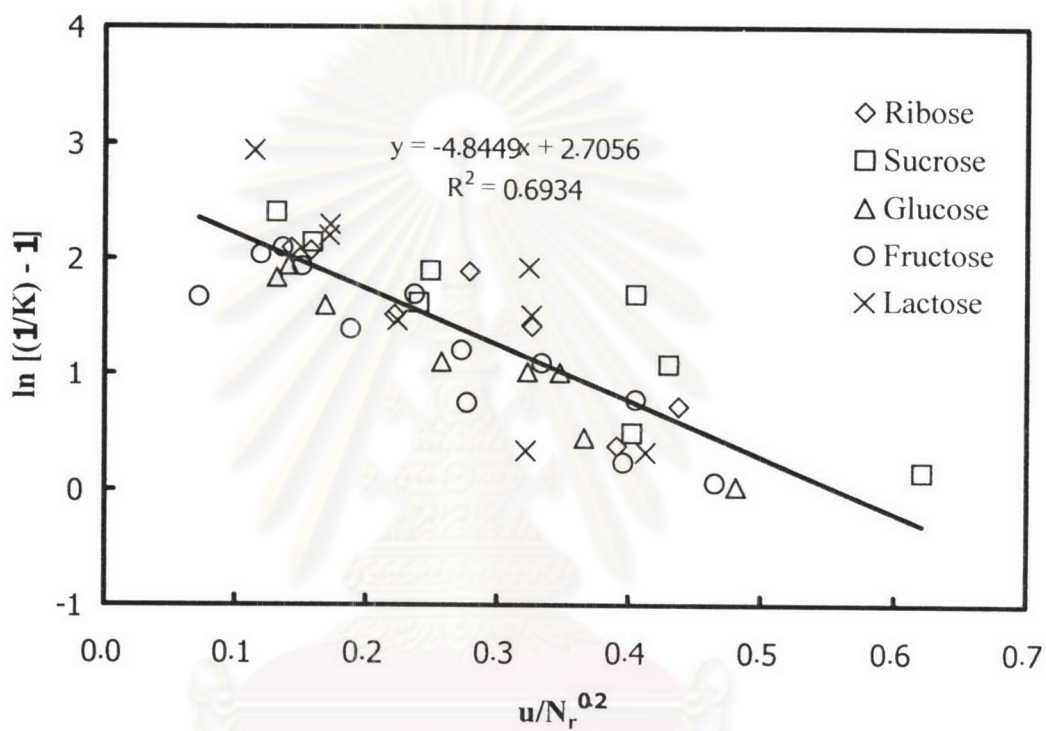
Fig. 4.15 Effects of the advance rate of ice front (u) and the stirring speed (N_r) on effective partition coefficient (K) of the non-ionic solutions at the concentration of 5.0% (w/w)
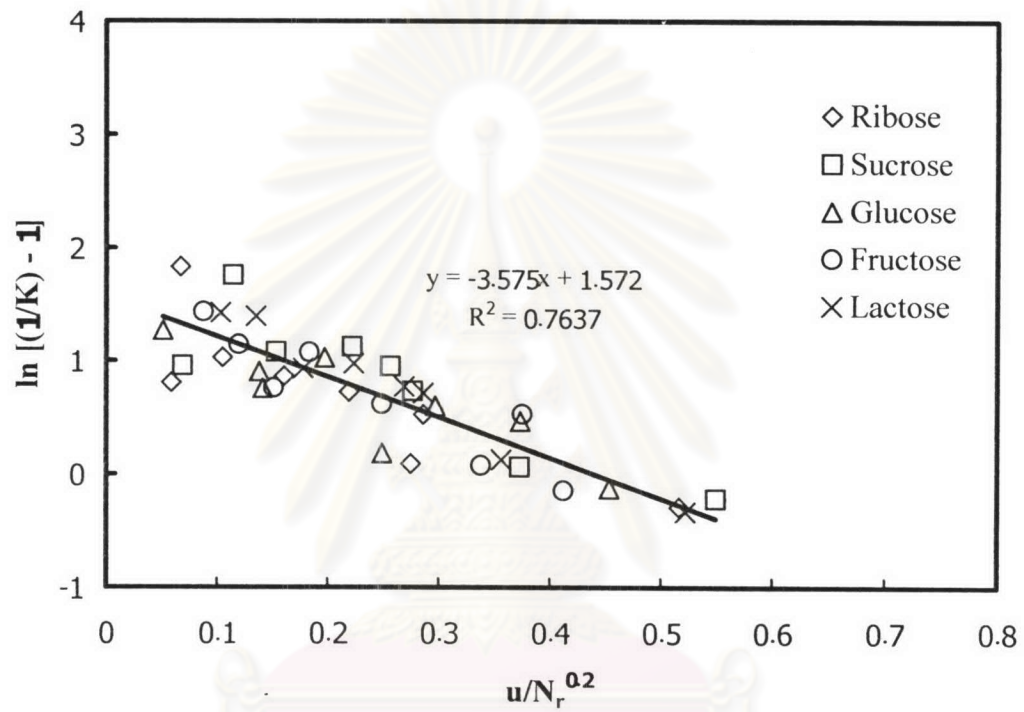
Fig. 4.16 Effects of the advance rate of ice front (u) and the stirring speed (N_r) on effective partition coefficient (K) of the non-ionic solutions at the concentration of 10.0% (w/w)
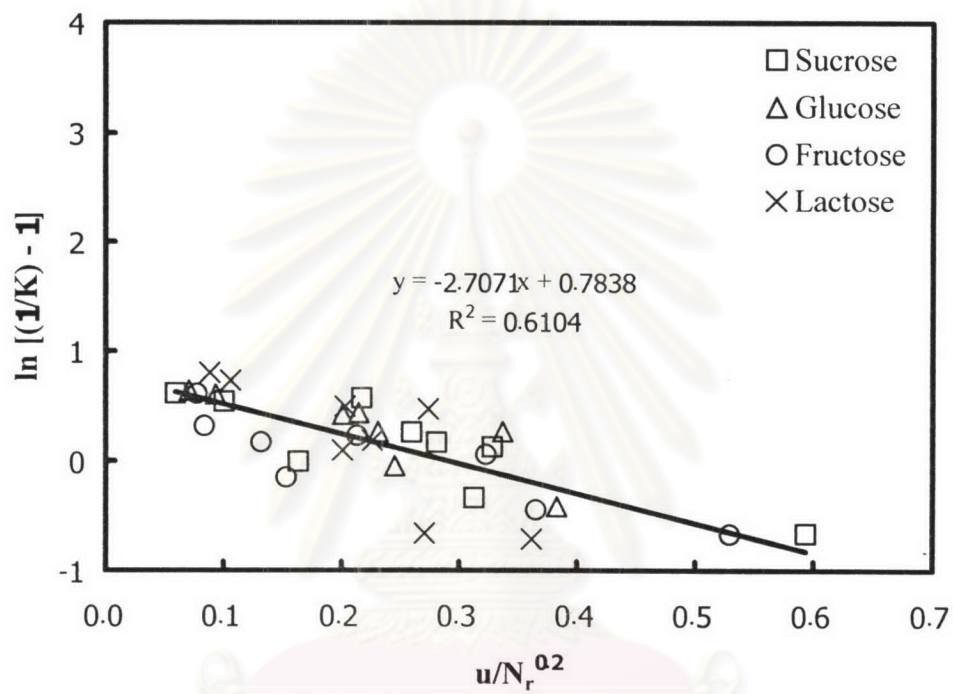
Fig. 4.17 Effects of the advance rate of ice front (u) and the stirring speed (N_r) on effective partition coefficient (K) of the non-ionic solutions at the concentration of 20.0% (w/w)
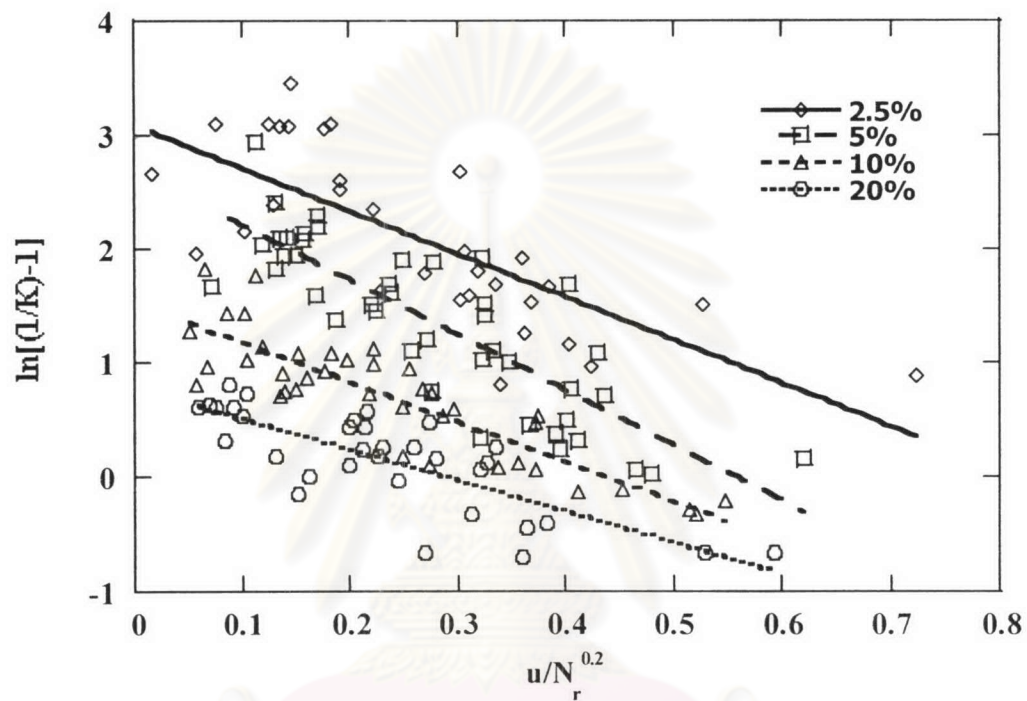
Fig. 4.18 Effects of the initial concentration (C_0) of the non-ionic solutions and the operating conditions on the effective partition coefficient (K)

4.2.3 Determination of the Limiting Partition Coefficient (K_0) of a Non-ionic Solute Based on the Concentration Polarization Model

From Figure 4.18, a y-intercept of each line can be obtained (following the same method described in Section 4.1.3) as follows: 3.10, 2.71, 1.53, and 0.78 for the solutions with the concentrations of 2.5, 5, 10, and 20% (w/w), respectively. From these y-intercepts, K_0 could be calculated, and the K_0 values of the solutions with the concentrations of 2.5, 5, 10, and 20% (w/w) were 0.04, 0.06, 0.18, and 0.31, respectively. The relationship between K_0 and the initial concentration (C_0) of the solution is shown in Figure 4.19.

It was found, from Figure 4.19, that an increase in C_0 caused K_0 to increase. This resulted from the depression of freezing point and a decrease in the efficiency of the mass transfer of solute molecules, discussed earlier.

When K_0 and C_0 were known, the phase equilibrium of each sugar can be calculated, as illustrated in Figure 4.20.
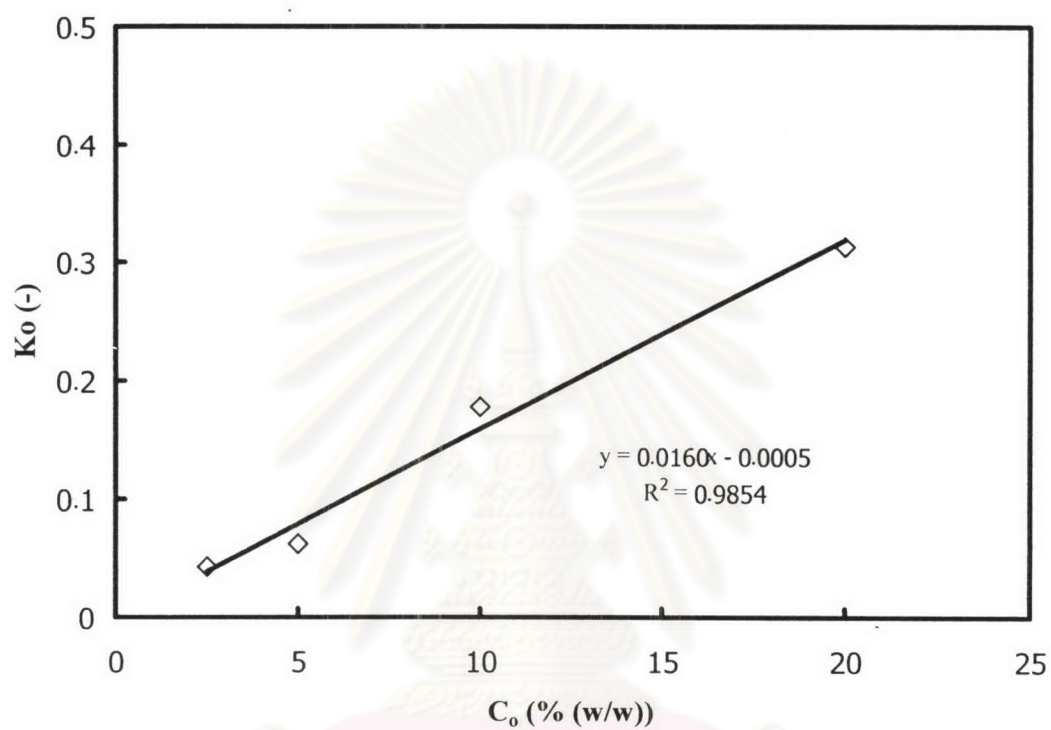
Fig. 4.19   Effect of the initial concentration (C_0) on the limiting partition coefficient (K_0)
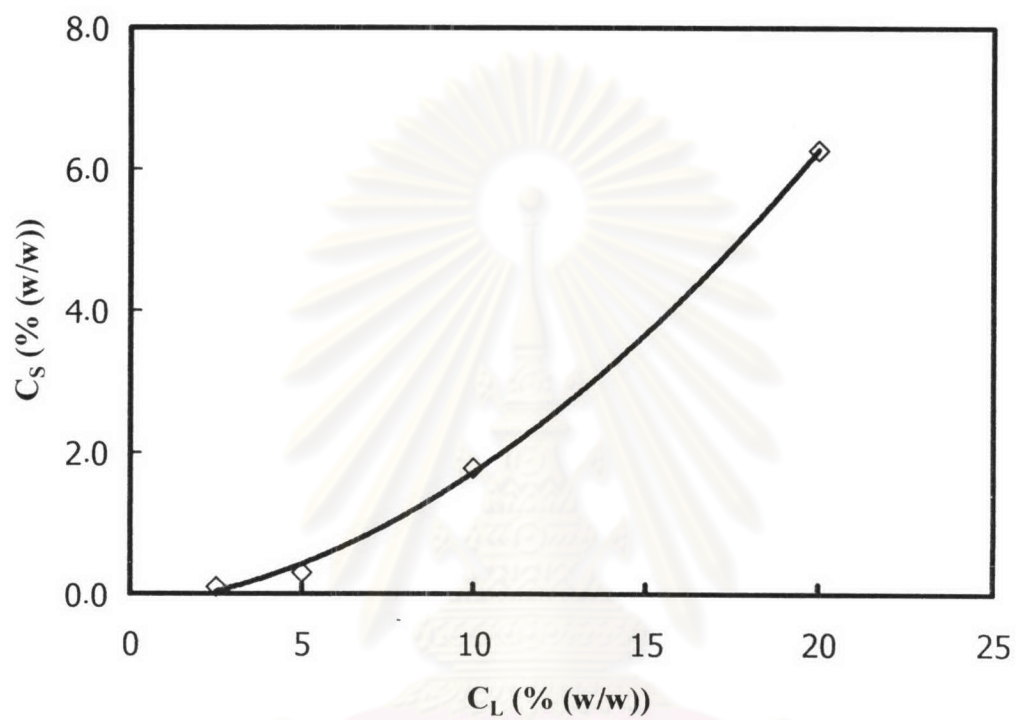
Fig. 4.20 A phase equilibrium plot of the non ionic solutions.

4.3   An Investigation of Factors Affecting the Efficiency of the Progressive Freeze-concentration on the Colloidal Solutions.

    4.3.1 <u>Effects of the Operating Conditions and the Initial Concentration (C_0) of the Colloidal Solutions on the Effective Partition Coefficient (K)</u>

        Following Eq (4.1), the relationship between $u/N_r^{0.2}$ and $\ln[(1/K) - 1]$ is plotted, as shown in Figure 4.21. Since R^2 from the figure is relatively low (= 0.1726), it was assumed that the operating conditions did not affect the K values of the solutions. Additionally, the K value was slightly affected by the initial concentration of the solution.
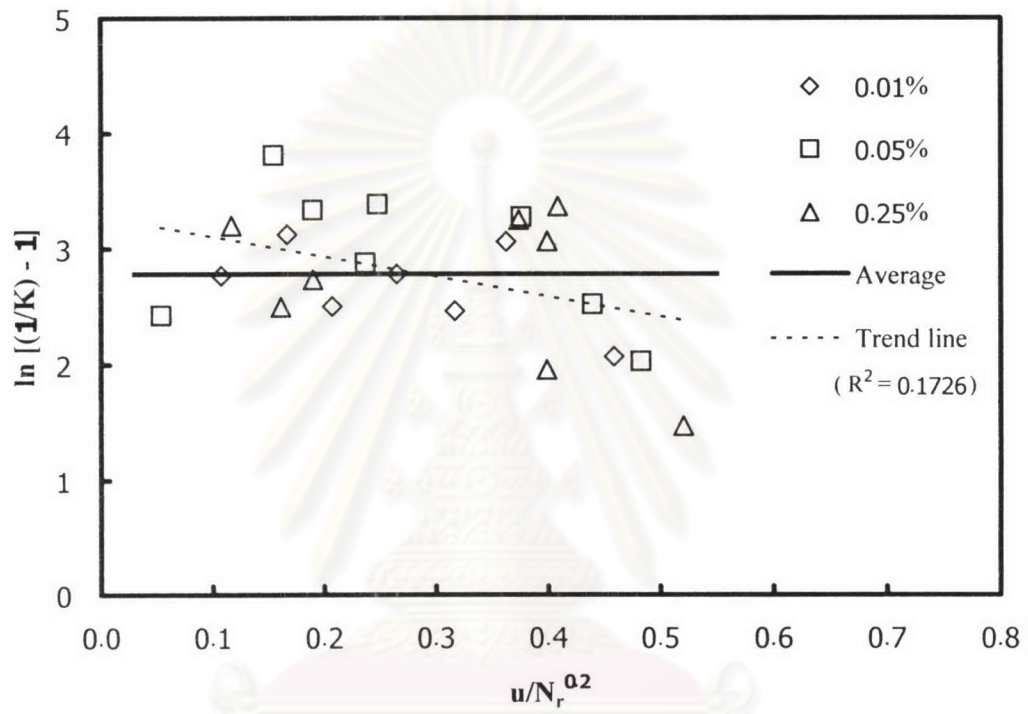
Fig. 4.21 Effects of the initial concentration (C_0) of the colloidal solutions and the operating conditions on the effective partition coefficient (K).

4.3.2 Effects of the Colloidal Molecular Weight (M.W.) and the Operating Conditions on the Effective Partition Coefficient (K) of the Colloidal Solutions

Figure 4.22 illustrates the effects of the molecular weight of dextran (M.W. 9,000 and 100.000) and blue dextran (M.W. 2,000,000), and of the operating conditions on the K value during the progressive freeze-concentration. Similar to the previous section, since R^2 is relatively low (= 0.0789), it is assumed that the molecular weight of the colloidal solution and the operating conditions have no effect on the K value during the progressive freeze-concentration.

Since dextran is a non-ionic polymer, it cannot form an ionic bond with water. Hence, when liquid water is frozen, dextran molecules in water is rejected from the ice layer by the advancing surface of a growing ice crystal. Additionally, since the molecules of dextran are large, it is unlikely to be trapped in the ice layer. Accordingly, the operating conditions and the molecular weight of dextran did not affect the K value.
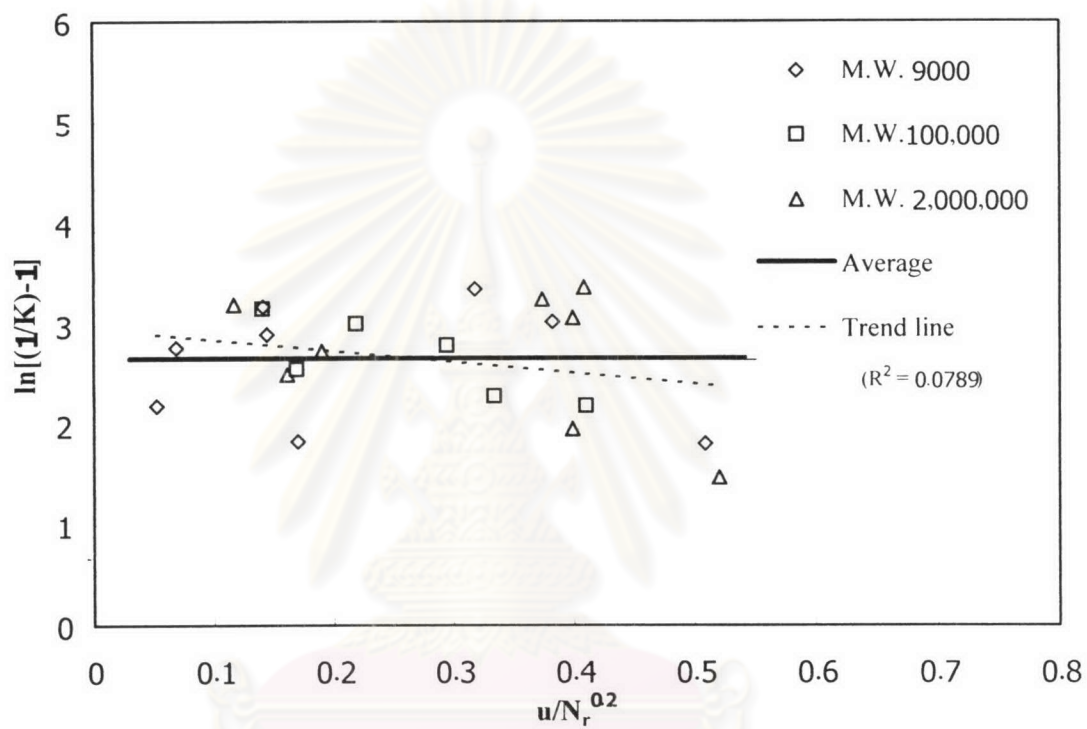
Fig. 4.22 Effects of the molecular weight of the colloidal solution and the operating conditions on the effective partition coefficient (K) of the colloidal solutions at the initial concentration of 0.25% (w/w)

The K value found in this study was, approximately, 0.06, which was considered to be small, or, in other words, it indicated that the efficiency of the phase partition was good. This then results in a very purified ice crystal, as shown in Figure 4.23.

Additionally, Since K_0 is constant, regardless of initial concentration and molecular weight, the phase equilibrium of dextran solution was found to be linear, as shown in Figure 4.24.

Before   After
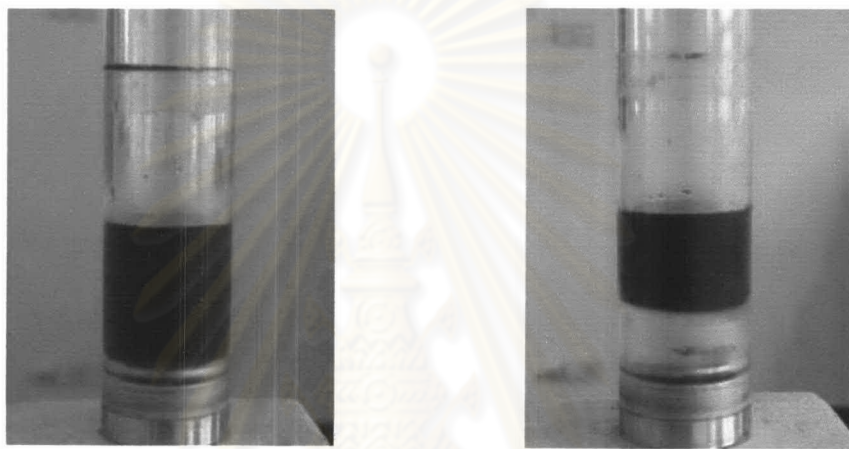

Fig. 4.23 Progressive freeze-concentration of blue dextran solution: before and
after the process.
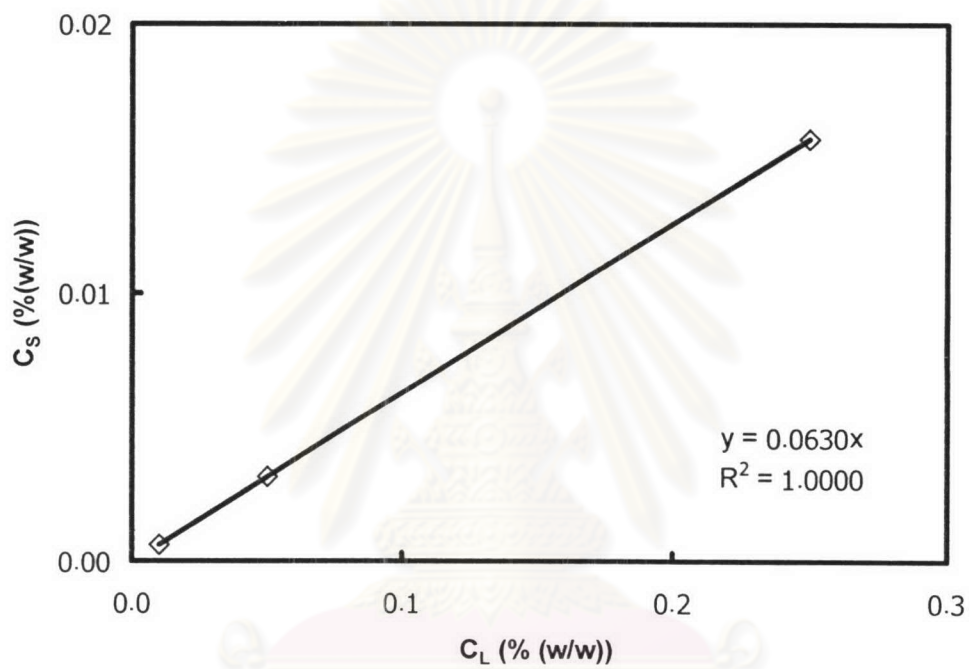
Fig. 4.24 A phase equilibrium plot of the colloidal solutions.

4.4 Determination of an a Constant of Ionic, Non-ionic, and Colloidal Solutions

As mentioned in Section 4.1.2, the constant a can also be obtained from the $\ln [(1/K) - 1] - u/N_r^{0.2}$ plot (slope of the plot is $-1/a$). The values of the constant a of ionic, non-ionic, and colloidal solutions are summarized in Table 4.1.

The values of a obtained in the present study were in the range of 0.10—0.37. However, the effects of the concentration and type of solution on the a value seem to be unclear. This is probably due to the fact that a is a constant for a mass transfer coefficient equation, described in Eq. (2.15), and, because of this, it is a complex function of, for example, viscosity, density, and diffusivity of a substance. Hence, it is difficult to determine the relationship between the type and concentration of solution and a.

Table 4.1   The a-values of ionic, non-ionic, and colloidal solutions

Solution	Sample	Co (% w/w)	a
Ionic	LiCl	0.5	0.16
		2.5	0.37
		4.0	0.29
	NaCl	0.5	0.33
		2.5	0.34
		10.0	0.33
	KCl	0.5	0.10
		2.5	0.25
		10.0	0.27
	CsCl	0.5	0.37
		2.5	0.21
		10.0	0.19
Non-ionic	Sugar	2.5	0.24
		5.0	0.21
		10.0	0.28
		20.0	0.37
Colloidal	Dextran	0.01	-
		0.05	-
		0.25	-