

Influence of Inorganic Salts on Aqueous Solubilities of Polycyclic Aromatic Hydrocarbons

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ABSTRACT

Setschenow constants of six alkali and alkaline earth metal-based electrolytes (i.e., NaCl, KCl, CaCl₂, K₂SO₄, Na₂SO₄, NaClO₄) for three polycyclic aromatic hydrocarbons (PAHs) (i.e., naphthalene, pyrene, and perylene) were investigated to evaluate the influence of a variety of inorganic salts on the aqueous solubility of PAHs. Inorganic salts showed a wide range of K_s values (L/mol), ranging from 0.1108 (NaClO₄) to 0.6680 (Na₂SO₄) for naphthalene, 0.1071 (NaClO₄) to 0.7355 (Na₂SO₄) for pyrene, and 0.1526 (NaClO₄) to 0.8136 (Na₂SO₄) for perylene. In general, the salting out effect of metal cations decreased in the order of Ca²⁺>Na⁺>K⁺. The effect of SO₄²⁻>Cl⁻>ClO₄⁻ was observed for anions of inorganic salts. The K_s values decreased in the order of perylene>pyrene>naphthalene for K₂SO₄. However, the order of decreasing salting out effect for NaCl, KCl, CaCl₂, and NaClO₄ was perylene>naphthalene>pyrene. Hydration free energy of the 1:1 and 2:1 alkali and alkaline earth metal-based inorganic salts solution was observed to have a meaningful correlation with Setschenow constants. Thermodynamic interactions between PAH molecules and salt solution can be of importance in determining the magnitude of salting out effect for PAHs at a given salt solution.

Key words: Polycyclic Aromatic Hydrocarbons, Solubility, Setschenow constant, Salting out effect, Hydration energy

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have received considerable attention because of their widespread occurrence, toxicity, and persistence in aquatic environment. The activity coefficient is one of the important parameters governing the environmental fate of PAHs. Aqueous solubility of an organic compound is inversely proportional to its activity coefficient in aqueous solution¹⁾. Hence, aqueous solubility can play a crucial role in the distribution of PAHs and their persistence in aquatic environments. In a variety of environmental fields, PAH solubility, which can be altered by the presence of inorganic salts, temperature, and co-solutes, has been identified as a key factor that affects or determines their bioaccumulation, biosorption, sorption to minerals and soils/sediments, and transport in aquatic environments^{1,2)}. Numerous researchers have reported that the presence of ionic species in water generally decreases the aqueous solubility of PAHs²⁻⁵⁾. These so-called "salting out" effects were first described by Setschenow⁶⁾. He established an empirical relationship between the solubility of organic compounds and the salt concentration as below:

$$\log \left[\frac{C_o}{C_{salt}} \right] = K_s \cdot [salt]_t \quad (1)$$

Where C_o (mol/L) is the solubility of the organic compound in distilled water, C_{salt} (mol/L) is the solubility of the organic compound in the salt solution, $[salt]_t$ (mol/L or mol/Kg) is the total molar or molal salt concentration and K_s (L/mol or Kg/mol) is the Setschenow or salting constant⁶⁾.

The salting out effect is of much significance in saline environments such as oceans, estuaries, salt lakes, and brackish aquifers, which has a relatively high concentration of a variety of salts. Several researchers showed that salting out effects in these types of saline aquatic systems can dramatically affect the sorption behavior, as well as other environmentally important reactions, of hydrophobic organic contaminants (HOCs)⁷⁻⁹⁾. Hence, the proper understanding various reactions in saline aquatic system requires knowledge of how salinity affects the activities/solubilities of neutral organic compounds.

Considerable effort has been made to examine the variation of PAH solubilities due to the presence of a variety of ionic species. The salting out effects of NaCl or seawater salts on the PAH solubilities are particularly important for the marine system because marine environment can cause a great

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modification of PAH solubilities. Therefore, many marine researchers have presented the Setschenow constants of various PAH molecules for NaCl or seawater salts.¹⁰⁻¹² However, relatively fewer studies were performed for the predominant alkali and alkaline earth metal-based inorganic salts in natural water system, which also can play an important role in controlling the fate and transportation of PAH molecules in surface water or ground water system. Even the scarce information on salting out effect for those inorganic salt species were provided only for limited PAH molecules such as naphthalene and phenanthrene. Little to no information is available for PAH molecules with relatively higher hydrophobic PAHs such as pyrene and perylene despite of their importance due to toxicity and persistence in environments.

The physicochemical characteristics of organic solutes and inorganic salts can play a critical role in determining the magnitude of salting out effect of organic solute for inorganic salt. For example, inorganic salts with higher hydration energy are expected to have higher salting out effect at a given organic solute because ions with higher hydration energies bind water more tightly, diminishing the available water to be able to dissolve organic solute. Hence, the information on the physicochemical characteristics of organic solute and inorganic salt can be of much importance in understanding the salting out effect of organic solute for inorganic salt. Nevertheless, little to no research has been conducted on the physicochemical properties of PAH molecules affecting the magnitude the K_s values at a given PAH and inorganic salt.

This study examined the influence of six common alkali and alkaline earth metal-based inorganic salts on the aqueous solubilities of three PAHs that vary widely in their aqueous solubilities. The results of this study were used to elucidate the mechanism of salting out effect of PAHs and investigate key factors affecting PAH Setschenow constants. In addition, the correlations between Setschenow constant and physicochemical properties of inorganic salts, organic solutes and solutions were studied to properly understand the salting out effect of PAHs in the presence of inorganic salts.

2. Material and Methods

2.1 Materials

Three PAHs, naphthalene (99%, Aldrich Chemical, Milwaukee, WI), pyrene (99%, Aldrich Chemical, Milwaukee, WI), and perylene (99%, Aldrich Chemical, Milwaukee, WI) were used as organic solutes. Sodium chloride (NaCl, crystals, 99.0%, EM Science, Gibbstown, NJ), potassium chloride (KCl, crystals, 99%, EM Science, Gibbstown, NJ), calcium chloride (CaCl₂, crystals, 99%, EM Science, Gibbstown, NJ), potassium sulfate (K₂SO₄, crystals, 99%, EM Science,

Gibbstown, NJ), sodium sulfate (Na₂SO₄, crystals, 99%, EM Science, Gibbstown, NJ), and sodium perchlorate (NaClO₄, crystals, 99%, EM Science, Gibbstown, NJ) were used in salting out experiment. All solutions were prepared using distilled deionized water (DDW) (Mega-Pure System MP-6A, Corning, NY) having a >18.0 mega cm⁻¹. PAH stock solutions were prepared by serial dilutions of naphthalene, pyrene, and perylene in methanol (HPLC Grade, Fisher Scientific, Fair Lawn, NJ).

2.2 PAH solubility experiments

PAH solubility experiments for various inorganic salts were conducted in twenty-five milliliter glass centrifuge tubes with Teflon-lined screw caps. For naphthalene, lead foil was placed onto the inner face of the Teflon-lined screw caps to minimize volatilization losses. The glass centrifuge tubes were prepared for use by soaking in methanol overnight, soaking in nitric acid at least overnight, and then rinsing with DDW. Inorganic salt solutions were prepared at more than three different concentrations, and then twenty milliliters of each solution was added to a centrifuge tube. Replicate samples were spiked with 20 μL of a particular PAH stock solution, which result in initial aqueous PAH concentrations of approximately four times higher than the expected PAH solubility limit even after accounting for sorption to the centrifuge tube walls and Teflon liners. The small volume of methanol added (volume fraction of 0.001) had no effect on PAH solubilities¹. All samples were then agitated on a temperature-controlled (20±0.1°C) orbital shaker at 375 rpm for 24 hours. After equilibration, the batch reactors were centrifuged at 7000 rpm in temperature-controlled centrifuge for 1 hour to separate the over-saturated PAH solids. Aliquots (5 mL) of the sample supernatants were transferred to 40-mL glass amber vial and then mixed with methanol at a 1:1 volume ratio to prevent further PAH sorption to glassware and the fluorescence cell during analysis. PAH concentrations in methanol-water mixtures were determined by fluorescence spectroscopy (Photon Technology International, Inc., Brunswick, NJ) using external standards. The excitation/emission wavelengths used for naphthalene, pyrene, and perylene quantification in the methanol-water mixtures were 276/320, 336/374 and 433/469 nm, respectively. Setschenow constants, K_s , were determined from the slope of the line obtained by plotting $\log(C_o/C_{salt})$ versus $[\text{salt}]_i$ in accordance with equation 1.

3. Results and Discussion

3.1 Salting effects of PAHs in salt solutions

Solubilities of naphthalene, pyrene, and perylene in distilled water were determined at 20°C, and these values are shown in Table 1 along with other physicochemical properties. The

Table 1. Physicochemical Properties of PAHs and Aqueous Solubilities of PAHs in Distilled Water

PAH	MW ^a (g/mol)	MV ^b (mL)	HSA ^c (Å ²)	Aqueous Solubility		N ^e
Naphthalene	128.2	125.0	155.8	24.7 ± 1.2 mg/L	193 ± 9.1 μM	22
Pyrene	202.3	171.5	213.0	90.6 ± 1.8 μg/L	447.8 ± 9.1 μM	10
Perylene	252.3	202	251.5	72.1 ± 2.1 μg/L	286 ± 8 pM	14

^aMolecular weight values from ref. 15.^bMolar volume values from ref. 16.^cHydrophobic surface area values from ref. 17.^dMeasured at 20°C in distilled, deionized water (DDW). Values shown are ± standard error.^eNumber of data point used.**Table 2.** Molar Concentration-based Setschenow Constants (K_s) for PAHs in various Aqueous Salts

PAHs	Salts	K_s (L/mol) ^a	R ²	N ^b	log C_o (nmol/L) ^c
Naphthalene	DDW ^d	n.a. ^e	n.a.	22	5.2864
	NaCl	0.2220 ± 0.008	0.9995	10	5.2861 ± 0.0049
	NaClO ₄	0.1108 ± 0.0008	0.9972	10	5.0377 ± 0.0055
	Na ₂ SO ₄	0.6680 ± 0.0043	0.9984	10	5.3097 ± 0.0069
	KCl	0.1992 ± 0.0008	0.9995	10	5.3033 ± 0.0030
	K ₂ SO ₄	0.6417 ± 0.0035	0.9985	10	5.3126 ± 0.0051
	CaCl ₂	0.3413 ± 0.0016	0.9989	10	5.3200 ± 0.0124
Pyrene	DDW	n.a.	n.a.	10	2.6511
	NaCl	0.2085 ± 0.0010	0.9998	10	2.6419 ± 0.0044
	NaClO ₄	0.1071 ± 0.0012	0.9950	7	2.6802 ± 0.0031
	Na ₂ SO ₄	0.7355 ± 0.0053	0.9983	10	2.6540 ± 0.0084
	KCl	0.1914 ± 0.0009	0.9994	10	2.6544 ± 0.0043
	K ₂ SO ₄	0.7247 ± 0.0029	0.9994	10	2.6469 ± 0.0039
	CaCl ₂	0.2175 ± 0.0011	0.9993	10	2.6079 ± 0.0029
Perylene	DDW	n.a.	n.a.	14.	-0.5436
	NaCl	0.2649 ± 0.0038	0.9954	6	-0.5451 ± 0.0299
	NaClO ₄	0.1526 ± 0.0031	0.7360	10	-0.4954 ± 0.0070
	Na ₂ SO ₄	0.6260 ± 0.0066	0.9967	10	-0.5524 ± 0.0124
	KCl	0.2261 ± 0.0037	0.9977	5	-0.5786 ± 0.0162
	K ₂ SO ₄	0.8136 ± 0.0081	0.9989	10	-0.4850 ± 0.0421
	CaCl ₂	0.3481 ± 0.0020	0.9993	10	-0.4212 ± 0.0114

^aObtained by linear regression of the equation $\log(C_o/C_{salt}) = K_s[\text{Salt}]_i$. values are ± standard error.^bNumber of data points in the regression.^cEstimated aqueous solubility at 20°C, obtained by linear regression of the equation $\log(C_o) = -\log(C_{salt}) + K_s[\text{Salt}]_i$. values are ± standard error.^dDDW: Distilled Deionized Water. values are average of the measured samples from Table 1.^en.a., not applicable.

solubility experiments of naphthalene, pyrene, and perylene in salt solutions were conducted to obtain the PAH solubilities at 20°C. The measured K_s values of six alkali and alkaline earth metal-based salts (i.e. NaCl, KCl, CaCl₂, K₂SO₄, Na₂SO₄, and NaClO₄) on PAHs are listed in Table 2. The results plotted as $\log(C_o/C_{salt})$ versus salt concentration at 20°C are represented in Fig. 1, 2 and 3, which demonstrate the effects of salt concentration on the aqueous solubility of naphthalene, pyrene, and perylene, respectively.

The results of solubility experiment in Table 2 show a wide range of K_s values (L/mol), ranging from 0.1108 (NaClO₄) to 0.6680 (Na₂SO₄) for naphthalene, 0.1071 (NaClO₄) to 0.7355 (Na₂SO₄) for pyrene, and 0.1526 (NaClO₄) to 0.8136 (Na₂SO₄)

for perylene. Each inorganic salt exhibited significantly different K_s value. In general, our K_s values compared very well with the limited number of reported values available in the literature^{4,10}. For example, Gordon and Thorne⁴) reported that the K_s values of NaCl and KCl for naphthalene were 0.220 and 0.186 (L/mol), respectively. Xie *et al.*¹⁰) obtained 0.332, 0.695 and 0.624 (L/mol) of K_s values for naphthalene/CaCl₂, naphthalene/Na₂SO₄ and naphthalene/K₂SO₄, respectively.

Upon examining the K_s values in Table 2, one can see that salting out effects occurred in the order of Ca²⁺>Na⁺>K⁺ and SO₄²⁻>Cl⁻>ClO₄⁻. For example, supposing that common ions have the same effect on K_s (L/mol), the effect of Na⁺>K⁺ for NaCl and KCl was shown with respect

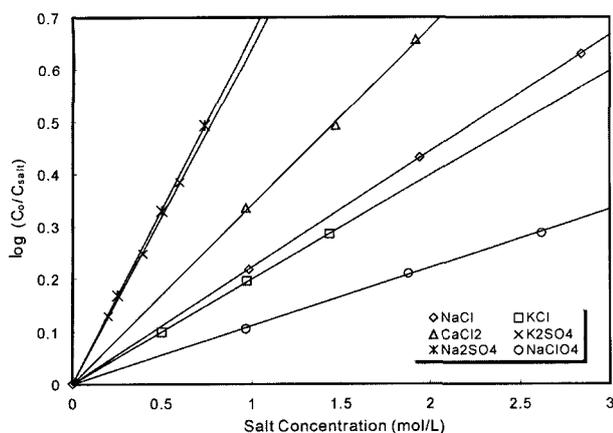


Fig. 1. Effects of inorganic salt concentration on the aqueous solubility of naphthalene.

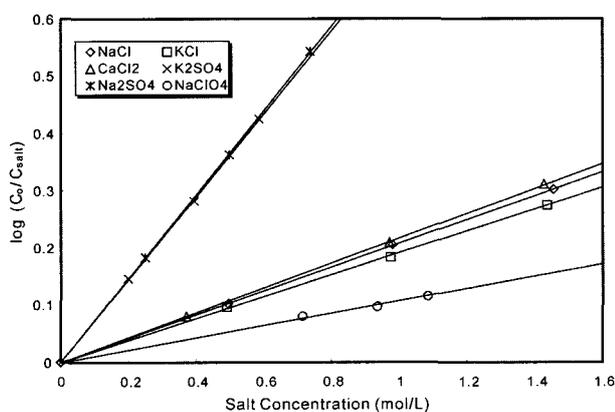


Fig. 2. Effects of inorganic salt concentration on the aqueous solubility of pyrene.

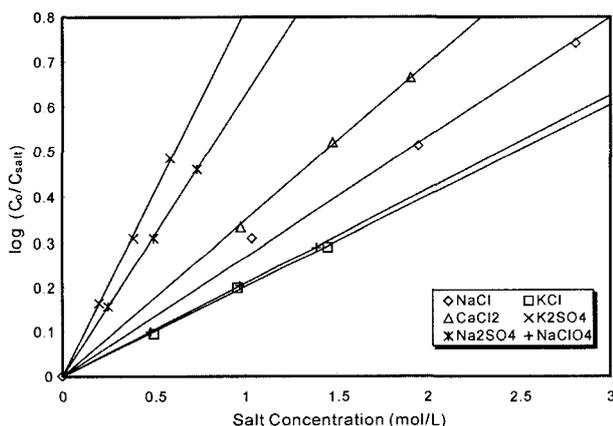


Fig. 3. Effects of inorganic salt concentration on the aqueous solubility of perylene.

to the solubility of naphthalene, pyrene, and perylene. The effect of $\text{Ca}^{2+} > \text{Na}^+$ was also observed for CaCl_2 and NaCl with respect to the PAHs. For NaClO_4 and NaCl , the salting

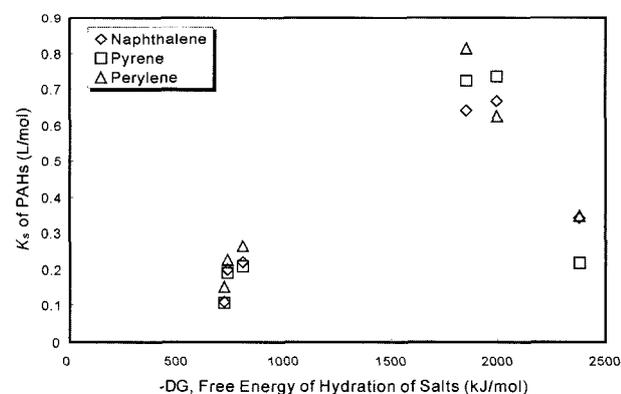
out effects decrease in the order $\text{Cl}^- > \text{ClO}_4^-$. The comparison of K_s values of Na_2SO_4 and NaCl showed the effect of $\text{SO}_4^{2-} > \text{Cl}^-$. This ordering of cations and anions is consistent with previous reports^{10,13}. Although there exist a variety of inorganic salts in natural seawater, the main solute component of seawater is known to be NaCl salt¹¹. Xie *et al.*¹⁰ reported that K_s values of organic compounds were similar for natural or artificial and NaCl solution. Their finding suggests that the solubilities of the organic solutes in natural seawater can be predicted using the experimental K_s values of organic compounds only for NaCl salt solution. Hence, the information on the K_s values of PAHs for NaCl salt obtained in this study can be widely used to simply estimate the PAH solubilities in marine aquatic environments such as ocean.

3.2. Mechanism and factors controlling salting effect of PAHs in salt solutions

Only a few attempts have been made to elucidate the mechanism and major physicochemical factors controlling salting out effect of organic compounds in the presence of electrolytes. McDevit and Long¹³ observed that Setschenow constants differed significantly among various electrolytes on the solubility of benzene in aqueous solutions. They suggested a mechanism of the salting out effect using the hypothesis that the salt ions in solution so strongly bind water into their hydration shell that the tightly bound water cannot form cavities to accommodate organic compounds. Based on their theory, the hydration energy seems to be able to provide a reasonable explanation for the fact that different inorganic salts show different salting out effects on a given compound. Ions with higher hydration energies bind water more tightly, thereby diminishing the available water to be able to dissolve organic compounds such as PAHs. Hence, ions with higher hydration energies might be expected to have larger K_s values than those with lower hydration energies because of the decreased solubility of PAH in the presence of ions with higher hydration energy. However, very little research has been presented to show the correlation of salting out effect with hydration energy of electrolytes. To evaluate the feasibility of application of hydration energy theory to Setschenow constants of electrolytes, the hydration free energy and Setschenow constants for various electrolytes were quantitatively compared in Table 3. The comparison for hydration free energy of all ion species in Table 3 demonstrates the magnitude of hydration free energy ($-\Delta G$) are in good agreement with the expected order of salting out, $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{ClO}_4^-$. Fig. 4 shows the correlation between log hydration free energy and log K_s values of various inorganic salt for a given PAH. In Fig. 4, the 1:1 and 2:1 alkali and alkaline earth metal-based inorganic salts with exception for 1:2 inorganic salt, CaCl_2 showed a

Table 3. Enthalpies, Entropies and Free Energies of Hydration and Setschenow Constants (K_s) for Alkali and Alkaline Earth Metal-based Electrolytes at 20°C^a

Species	Hydration Volume (cm ³ /mol) ^{ab}	(-ΔH) Hydration Enthalpies (kJ/mol) ^a	(ΔS) Hydration Entropies (J/K·mol) ^a	(-ΔG) Hydration Free Energy (kJ/mol) ^a
Cations				
Na ⁺		405	59	422
K ⁺	-1.2	321	101	351
Ca ²⁺	9.0	1592	53	1608
Anions				
Cl ⁻	-17.9	369	55	385
ClO ₄ ⁻	17.8	244	182	297
SO ₄ ²⁻	44.1	1145	17	1150
	14.0			
Salts	-ΔG (kJ/mol) ^c	Naphthalene K_s (L/mol)	Pyrene K_s (L/mol)	Perylene K_s (L/mol)
NaCl	807	0.2220	0.2085	0.2469
NaClO ₄	719	0.1108	0.1071	0.1357
KCl	736	0.1992	0.1914	0.2105
Na ₂ SO ₄	1994	0.6680	0.7355	0.6260
K ₂ SO ₄	1852	0.6417	0.7247	0.8136
CaCl ₂	2378	0.3413	0.2175	0.3027

^aObtained from ref. 18.^bPartial molal hydration volumes (cm³/mol) for hydrated ions (relative to zero for the proton).^cCalculated from data of each ion.**Fig. 4.** Correlation of hydration free energy ($-\Delta G$) with the Setschenow constants of PAHs.

general tendency of increasing effect on Setschenow constant as its hydration free energy increased. The meaningful correlation of hydration free energy with Setschenow constants suggests that the inorganic salts with higher thermodynamic energy are expected to have larger magnitude of salting out effects. In addition, this finding might provide a plausible explanation for the reason that different salting out effect occur depending on the species of inorganic salts. More research is required to elucidate the reason for the non-applicability of 1:2 inorganic salt (CaCl₂) to the correlation between hydration energy and salting effect.

McDevit and Long's theory states that an increase in the liquid molar volume of the nonelectrolyte solute increase K_s values. A few researchers demonstrated the experimental results supporting the theory of McDevit and Long. For example, May⁵⁾ quantified the values of Setschenow constants for a series of PAHs in NaCl solutions at 25°C. His experimental data exhibited that there was a proportional relation between Setschenow constant and molar volume. However, in contrast to their theory, several researchers demonstrated that the theory might break down for some experimental condition (e.g., specific temperature range)^{2,12,14}. Schwarz¹⁴⁾ suggests that the theory of McDevit and Long may hold only for a limited temperature range (e.g., temperatures condition above 25°C), breaking down for condition below 25°C. He measured the solubilities of naphthalene, pyrene, and benzo(e)pyrene in 0.5 M NaCl solution. In his experiments, the K_s of pyrene increases with an augment in temperature while those of naphthalene and benzo(e)pyrene decrease with an increase in temperature. The independence of temperature on Setschenow constant has been studied by other a few researchers^{2,12}. Whitehouse^{2,12)} obtained experimental results contrary to the theory of McDevit-Long for the Setschenow constant of PAHs over the studied temperature range. His study showed there was no definite correlation between surface area and Setschenow constant at a given certain temperature range. Similar trend was

observed in this study. As shown in Tables 2, in which the solubility experiment was conducted at 20°C, K_s values decrease in the order of perylene > pyrene > naphthalene for K_2SO_4 , consistent with the theory of McDevit and Long. However, the order of decreasing salting out effects for NaCl, KCl, $CaCl_2$, and $NaClO_4$ was perylene > naphthalene > pyrene, seemingly in contrast to the theory developed by McDevit and Long. These results could suggest that the surface area of solute might not be only factor to determine the order of Setschenow constant for the series of PAHs. Although the abnormal effect of temperature on Setschenow constant is not clearly understood, thermodynamics among organic solute, salt solution, and water molecules might somehow affect the salting out effect. The complex thermodynamic interactions between the organic solute and the cavity of solution might account for the fact that the theory of McDevit and Long break down for a certain temperature zone. When hydrophobic organic molecule, which is dissimilar to polar water solution, mixes in water solution, various enthalpic and entropic processes may greatly contribute to the excess free energy of solution¹. These enthalpic and entropic processes are closely involved in a bonding phenomenon between the organic solute and the cavity of solution because the organic solute isolated from pure liquid phase inserted into the cavity created in water and formed into more stable bond with water. Hence, temperature, which is strongly related to the enthalpy and entropy of solution, might cause an abnormal effect on salting out phenomenon. More intensive research has to be performed to elucidate why the order of Setschenow constants for a series of PAHs varies according to temperature.

4. Conclusions

Molar-based Setschenow constants (K_s) for six alkali and alkaline earth metal-based inorganic salts were determined at 20°C to evaluate their influence on the solubilities, and thus the aqueous activity coefficients, of three PAHs. Based on the experimental results from this study, the following conclusions are offered.

1. The six alkali and alkaline earth metal-based salts showed a wide range of K_s values (L/mol), ranging from 0.1108 ($NaClO_4$) to 0.6680 (Na_2SO_4) for naphthalene, 0.1071 ($NaClO_4$) to 0.7355 (Na_2SO_4) for pyrene, and 0.1526 ($NaClO_4$) to 0.8136 (Na_2SO_4) for perylene.

2. The salting out effect of metal cations decreased in the order of $Ca^{2+} > Na^+ > K^+$. The effect of $SO_4^{2-} > Cl^- > ClO_4^-$ was observed for anions of inorganic salts.

3. The expected trend of increased salting out effect with increasing solute size was not observed from most of these common inorganic salts. The K_s values decreased in the order

of perylene > pyrene > naphthalene for K_2SO_4 . However, the order of decreasing salting out effect for NaCl, KCl, $CaCl_2$, and $NaClO_4$ was perylene > naphthalene > pyrene.

4. Hydration free energy of the 1:1 and 2:1 alkali and alkaline earth metal-based inorganic salts has a meaningful correlation with Setschenow constants. Hydration free energy of salt solution can be an important physicochemical factor that might account for different magnitude of salting out effect according to the species of salt in the solutions.

5. The surface area of organic solute might not be only factor to determine the order of Setschenow constant for the series of PAHs. Enthalpic and entropic processes between PAH molecules and salt solution can be of significance in determining the magnitude of salting out effect for a series of PAHs at a given salt solution.

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