Monte Carlo Simulation Study of Solvent Effect on Δlog K_s of Rb$^+$ and K$^+$ Ion to 18-Crown-6

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The solvent effects on both of the relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 and Δlog K_s (the difference of stability constant of binding) have been investigated using a Monte Carlo simulation of statistical perturbation theory in several solvents. Comparing the relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 in H$_2$O (TIP4P) and CH$_3$OH in this study with the published works, there is a good agreement among the studies. The Born's function [i.e., $(1 - 1/\epsilon)$, where ϵ is the dielectric constant] of the solvents and the differences in solvation dominate the differences in the relative free energies of binding and Δlog K_s.

1. Introduction

The study of host−guest interactions[1−4] has received an increasing interest, since the discovery of crown ether by Perdersen.[5] These complexing agents display a wide range of binding specificities, and the association properties of crown ethers with alkaline cations have been mainly described in terms of similarities between the cation size and the size of the inner hole of the crown ether.[2] The selectivity of 18-crown-6 (1,4,7,-10,13,16-hexaoxacyclooctadecane) depends on the way in which six oxygen atoms are arranged to interact with guest molecules. In addition to the host−guest interaction, factors in the selective extraction of any host species include the relative free energy of desolvation of the guest molecules and the free energy of organizing the host into a suitable conformation with remote substitution for binding.[6]

Understanding the phenomena related to the solvation of cation ionophores has been an important quest in chemical physics and of course in many related fields where this phenomenon has a relevant role. Because of the large number of particles forming these systems and to the variety of different interactions established, computer simulations represent particularly adequate theoretical tools for understanding and predicting the physicochemical properties of those solutions at the microscopic level.[7−9] Interaction between cations and crown ethers in solution is widespread, and the ability of the crown ether to select one cation over the other in solution is important in environmental research.[10] It is known that solvation plays a major role in ion selectivity processes by influencing the stability and the nature of host−guest complexes.

To address the phenomena themselves and their challenges, we need the information of selectivity of 18-crown-6 for alkali metal cations in solution. This can be obtained from the relative free energies of 18-crown-6 complexation with metal cation mutation in solution.

Several statistical mechanical procedures have evolved for computing free energy differences. Two particularly promising approaches are umbrella sampling[11−15] and a perturbation procedure[16,17] in which one ion is mutated into the other.

Especially, the ability to accurately calculate solvation free energies of molecules using the perturbation procedure is one of the important and recent developments in computational chemistry.[18]

It is known that solvent effects often play an important role in determining equilibrium constants, transition states and rates of reactions, π-facial selectivity,[19] conformations, and the other quantities of chemical, chemical physics, and biochemical interest. However, few studies of solvent effects on both the relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 and Δlog K_s are available.

In this study, I have investigated the solvent effect on the relative stability constant of binding of K$^+$ and Na$^+$ ion to 18-crown-6, using Monte Carlo simulations of statistical perturbation theory (SPT).

H$_2$O (TIP3P, SPC/E, TIP4P models), CHCl$_3$, CH$_3$CN, tetrahydrofuran (THF), CH$_3$OH, CCl$_4$, MeCl$_2$, MEOME, and C$_3$H$_8$ were selected as solvents.[20] Experimental and molecular dynamic simulation studies of the relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 in water have been reported.[4,6] However, the study to calculating Δlog K_s as well as the relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 in several solvents is not available. The fundamental and theoretical approach to computing solvent effects on differences of log K_s (stability constant) as well as the relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 are, for the first time, explored based on fluid simulations at the atomic level for those by Monte Carlo simulation of SPT in this study. This study provides additional interests of the solvent effect[21] on equilibrium constants, transition states, rates of the organic reaction,[22] and the other quantities of chemical, biochemical, and chemical physics interest.
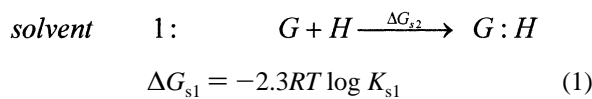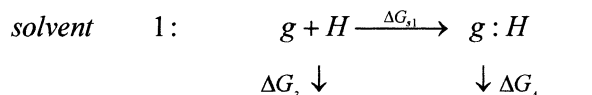
2. Computational Details

The procedure used here is similar to that employed to study refs 23−25. The modeled systems consisted of an ion and 18-crown-6 plus 250 solvent molecules in a cubic cell with periodic boundary conditions in the isothermal−isobaric ensemble at 25 °C and 1 atm. First, the Monte Carlo simulations are described, including a summary of the method for computing the relative free energy changes, and a brief discussion of the potential functions is given.

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2.1. Monte Carlo Simulations. The free energy changes were obtained via a series of five separate simulations with SPT in forward and backward directions.[18,26] To study the equilibrium thermodynamics of binding, we have used Monte Carlo simulations with the thermodynamic cycle perturbation theory and doublewide sampling.[24,26,27] In the notation of this method, the relative free energy of binding between guest G and g to the host H can be expressed as $\Delta\Delta G = \Delta G_{s2} - \Delta G_{s1} = \Delta G_4 - \Delta G_3$

$$solvent \quad 1: \qquad g + H \xrightarrow{\Delta G_{s1}} g : H$$

$$\Delta G_3 \downarrow \qquad\qquad \downarrow \Delta G_4$$

$$solvent \quad 1: \qquad G + H \xrightarrow{\Delta G_{s2}} G : H$$

$$\Delta G_{s1} = -2.3RT \log K_{s1} \tag{1}$$

$$\Delta G_{s2} = -2.3RT \log K_{s2} \tag{2}$$

Here, ΔG_s is the free energy of binding of guest to host and any thermodynamic state function and $\log K_s$ is the stability constant of guest to host.

From the cycle, eq 3 is obtained, which yields eq 4. The last expression associates the difference in $\log K_s$ values with the difference in the relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6[28] in the two solvents.

$$\Delta G_{s2} - \Delta G_{s1} = \Delta G_4 - \Delta G_3 \tag{3}$$

$$\Delta \log K_s = \log K_{s2} - \log K_{s1} = (\Delta G_{s2} - \Delta G_{s1})/2.3RT \tag{4}$$

In this study, the substitutions are H = 18-crown-6, g = K^+, and G = Rb^+. ΔG_{s1} and ΔG_{s2} are available from Monte Carlo simulations in which guest is binding to host in the solvents.

In this study, simulations were run for a coupling parameter, λ_i, which was used to smoothly transform 18-crown-6/Rb^+ ion complex ($\lambda = 0$) to 18-crown-6/K^+ ion complex ($\lambda = 1$). In this context, it is convenient to define a coupling parameter λ that allows the smooth conversion of system 0 to 1. Then, for many possible features ζ of the systems including geometrical and potential function parameters, eq 5 can be used to represent the mutation of system 0 to 1 as λ goes from 0 to 1.[23-26]

$$\zeta(\lambda) = \zeta_0 + \lambda(\zeta_1 - \zeta_0) \tag{5}$$

In this study, each simulation entailed an equilibration period for 4×10^6 configurations starting from equilibrated boxes of solvent, followed by averaging for 2×10^7 configurations. Little drift in the averages was found during the last 1×10^7 configuration.[23-25] Other details are that Metropolis and preferential sampling were employed, and the ranges for attempted translations and rotations of the solute and solvent molecules were adjusted to give a ca. 45% acceptance rate for new configurations.[23-25]

2.2. Potential Functions. The pair potential energy function of the optimized potential for liquid simulation (OPLS) force field is of the following form:[20]

$$E_{\text{total}} = \sum_{\text{bonds}} K_r(r - r_0)^2 + \sum_{\text{angles}} K_\theta(\theta - \theta_0)^2 +$$

$$\sum_{\text{torsions}} \frac{V_n}{2}[1 \pm \cos(n\phi - \gamma)] + \sum_{\text{nonbonded}} \left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{\epsilon r_{ij}} \right] f_{ij} \tag{6}$$

$$f_{ij} = 0.5 \text{ if } i,j \text{ are } 1,4; \text{ otherwise}, f_{ij} = 1.0$$

where K_r, K_θ, V_n, and φ are empirical parameters relating to bond, bond angle, and torsion angle. The ion and molecules are represented by interaction sites located on nuclei that have associated charge, q_i, and Lennard–Jones parameter σ_i and ϵ_i. One of the standard rules is used such that $A_{ij} = (A_{ii}A_{jj})^{1/2}$ and $C_{ij} = (C_{ii}C_{jj})^{1/2}$. Furthermore, the A and C parameters may be expressed as $A_{ii} = 4\epsilon_i\sigma_i^{12}$ and $C_{ii} = 4\epsilon_i\sigma_i^6$ where σ and ϵ are the Lennard–Jones radius and energy terms and i and j indices span all of the 18-crown-6, solvents, and water sites. In ref 6, Kollman et. al concluded that the additive force field model is adequate to describe energetics of cation complexation with 18-crown-6. In ref 29, we have also noted that the equation has been dominant with two-body potential functions that are parametrized to take the higher order interaction and polarization effect into account.

The OPLS potential parameters are used for solvents, and those are based on a united atom model,[22,20] but the TIP4P, SPC/E,[30] and TIP3P models have been used for water.[20] The 18-crown-6 is represented with the OPLS-AA force field.[20] The charges and Lennard–Jones parameters have been selected to yield correct thermodynamic and structural results of pure liquids.[20] In all of the calculations, the bond lengths, bond angles, and dihedral angles have been varied in simulations so that the statistical uncertainties for the computed values are within ($\pm 1\sigma$) fluctuations. The intermolecular interactions were spherically truncated at 8.5, 10, and 12.0 Å, depending on box sizes of solvents.[22,23] The cutoff correction to the solvent–solvent energy for nonaqueous solvents is applied to only Lennard–Jones potential functions.[20]

3. Results and Discussion

3.1. Relative Free Energies of Binding. To study the solvent effect on differences in stability constant ($\Delta\log K_s$) as well as the relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6, we have computed those in the three water models and in other solvents.

The calculated relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6 along with the experimental and computer simulation works are listed in Table 1. The reported statistical uncertainties for the computed values were within ($\pm 1\sigma$) fluctuations and were obtained from separate averages over 4×10^6 to 2×10^7 configurations. The ordering of computed relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6 (ΔG) in several solvents is $CCl_4 > C_3H_8 > CHCl_3 > CH_2Cl_2 > CH_3CN > H_2O$ (TIP4P) > THF > H_2O (TIP3P) > H_2O (SPC/E) > MEOME > CH_3OH. This comes about by the change in relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6 being more favorable in CH_3OH than in the polar and less polar or nonpolar solvents. In this study, we have noted that the intermolecular interactions depend on box sizes of solvents and the potential cutoff, but the results truncated at 8.5, 10, and 12.0 Å, depending on box sizes of solvents, are only listed in Table 1 for clarity.

Comparing relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6 in H_2O (TIP4P) in this study with those in refs 31 and 32, that of H_2O (TIP4P) in this study is -5.81 ± 0.13 kcal/mol, and those of H_2O in ref 31 and the experimental work in water[32] are -6.59 and -5.74 kcal/mol, respectively. There is good agreement among the studies considering both methods used to obtain the relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6 and standard deviations. In contrast to them, the relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6 in the other solvents are expected to be reliable.

TABLE 1: Relative Solvation Gibbs Free Energies (kcal/mol) and the Relative Binding Gibbs Free Energies (kcal/mol) in Several Solvents and Born's Function (1 − 1/ε) of Bulk Solvents

| solvent	ΔG (Rb$^+$ → K$^+$)[e]	ΔG (18-crown-6/Rb$^+$ → 18-crown-6/K$^+$)	$\Delta\Delta G$ of binding	1 − 1/ε
H$_2$O (SPC/E)	−5.19 ± 0.05	−6.66 ± 0.15	1.47	0.987
H$_2$O (TIP3P)	−5.57 ± 0.06	−6.38 ± 0.16	0.81	0.987
H$_2$O (TIP4P)	−5.00 ± 0.11	−5.81 ± 0.13	0.81	0.987
H$_2$O (rigid SPC)[a]	−5.40 ± 1.9			0.987
H$_2$O (LD-CS2)[b]	−5.5			0.987
H$_2$O (SPC)[c]	−5.4 ± 1.9	−6.59	1.19	0.987
H$_2$O exp[d]	−5.1	−5.74	0.64	0.987
CH$_3$CN	−5.06 ± 0.07	−5.75 ± 0.18	0.66	0.973
CH$_3$OH	−5.83 ± 0.08	−6.91 ± 0.15	1.07	0.963
CH$_3$OH exp[c]			1.04	0.963
CH$_2$Cl$_2$	−2.70 ± 0.05	−5.60 ± 0.01	2.90	0.888
THF	−4.99 ± 0.11	−6.37 ± 0.01	1.38	0.868
MeOMe	−4.86 ± 0.06	−6.53 ± 0.11	1.67	0.801
CHCl$_3$	−1.12 ± 0.03	−5.49 ± 0.11	4.37	0.792
CCl$_4$	−0.62 ± 0.03	−5.11 ± 0.10	4.49	0.552
C$_3$H$_8$	−0.28 ± 0.02	−5.08 ± 0.12	4.80	0.138

[a] Ref 37. [b] Ref 6. [c] Ref 31. [d] Ref 32. [e] Ref 24.

The relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 in H$_2$O (SPC/E) are smaller than those of H$_2$O (TIP3P) and H$_2$O (TIP4P). This difference could be explained by the difference of polarity among three water models.

3.2. Relative Binding Gibbs Free Energies. The relative binding Gibbs free energies of Rb$^+$ and K$^+$ ion to 18-crown-6 can be calculated using eq 3, and the published data of the relative free energies[31,32] are also listed in Table 1. The ordering of the relative binding Gibbs free energies in several solvents is C$_3$H$_8$ > CCl$_4$ > CHCl$_3$ > CH$_2$Cl$_2$ > MEOME > H$_2$O (SPC/E) > THF > CH$_3$OH > H$_2$O (TIP3P) = H$_2$O (TIP4P) > CH$_3$CN. This comes about by the change in relative binding Gibbs free energies being more favorable in CH$_3$CN than in the polar and less polar or nonpolar solvents. Note that the signs of the relative binding Gibbs free energies are positive in all solvents in Table 1. That is, 18-crown-6 binds K$^+$ more tightly than Rb$^+$ in all solvents, i.e., the selectivity of 18-crown-6 to K$^+$ is more favorable than to Rb$^+$ in all solvents. Because 18-crown-6 has a cavity radius ranging between 1.3 and 1.6 Å, it selectively binds K$^+$ over Rb$^+$ in all solvents where the cationic radii are 1.33 and 1.49 Å, respectively.[25b] In this study, the cations have one positive charge and the binding cores of the hosts consist of six oxygen atoms with large partial negative charges; electrostatic interactions are also expected to play an important role in the determining the cation binding ability of the 18-crown-6 system. A similar trend of the relative binding Gibbs free energies of Rb$^+$ and K$^+$ ion to 18-crown-6 has been observed in refs 6 and 25b.

The relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 and the relative binding Gibbs free energies vs Born's function [i.e. (1 − 1/ε), where ε is the dielectric constant of bulk solvent] of the solvents are plotted in Figure 1. As shown in Figure 1, the relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 and relative binding Gibbs free energies vs Born's function of the solvent decreased with increasing Born's function of solvents except CH$_3$CN, THF, and MEOME. This trend of relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 and relative binding Gibbs free energies could be explained by the differences in interaction between complex molecule and solvent molecule. Especially, the relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 in CH$_3$-CN, THF, and MEOME could be explained by the fact that the relatively stronger complex molecule−solvent molecule interactions exist in CH$_3$CN, THF, and MEOME solutions than in the other solutions even though Born's function of CH$_3$CN, THF,
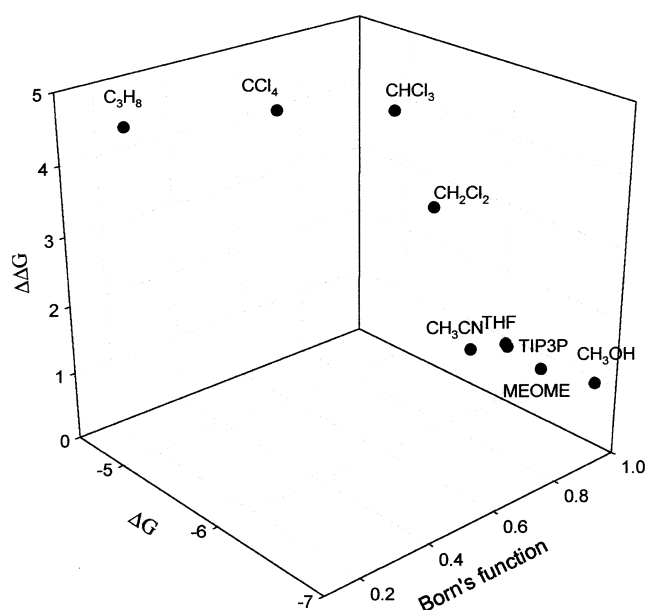
Figure 1. Plot of relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 (ΔG) and relative binding Gibbs free energies ($\Delta\Delta G$) vs Born's function of the solvent at 298 K and 1 atm.

and MEOME is small in value. The strong complex molecule− solvent molecule interactions in CH$_3$CN, THF, and MEOME solutions are due to the electron pair donor properties of the solvent molecules to ion, i.e., donor number (DN) of CH$_3$CN, THF, and MEOME established by Gutmann.[33]

Comparing relative binding Gibbs free energies in H$_2$O (TIP4P) and CH$_3$OH in this study with those in refs 31 and 32, those of H$_2$O (TIP4P) and CH$_3$OH in this study are 0.81 and 1.07 kcal/mol, those of H$_2$O in ref 31 and the experimental work in water[32] are 1.19 and 0.64 kcal/mol, and that of experimental work in CH$_3$OH[32] is 1.04 kcal/mol, respectively. In contrast to them, the relative binding Gibbs free energies in the other solvents are also expected to be reliable.

3.3. Relative Stability Constants. The differences in stability constant ($\Delta\log K_s$) of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 can be calculated by using eq 4. The signs of differences in stability constant ($\Delta\log K_s$) of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 are positive in all solutions. A positive sign of $\Delta\log K_s$ implies that 18-crown-6 binds K$^+$ more tightly than Rb$^+$ in all solution, i.e., the selectivity of 18-crown-6 to K$^+$ is more favorable than to Rb$^+$ in all solvents.

TABLE 2: Differences in the Binding Stability Constant of Rb$^+$ and K$^+$ Ion to 18-Crown-6

solvent	$\log K_{s2} - \log K_{s1}$	solvent	$\log K_{s2} - \log K_{s1}$
H$_2$O (SPC/E)	1.08	MeCl$_2$	2.13
H$_2$O (TIP3P)	0.59	THF	1.01
H$_2$O (TIP4P)	0.59	MEOME	1.23
exp (H$_2$O)^a	0.47	CHCl$_3$	3.21
CH$_3$OH	0.78	CCl$_4$	3.30
exp (CH$_3$OH)^a	0.76	C$_3$H$_8$	3.52
CH$_3$CN	0.48		

^{a} Ref 32.

TABLE 3: Structural Properties of 18-Crown-6/Rb$^+$ and 18-Crown-6/K$^+$ Ion Complex in Several Solvents

solvent	18-crown-6/Rb$^+$ ion		18-crown-6/K$^+$ ion	
	R_{i-o} (Å)	CN	R_{i-o} (Å)	CN
H$_2$O(SPC/E)	3.1	3.1	2.9	2.6
H$_2$O(TIP3P)	2.9	2.7	2.7	2.2
H$_2$O(TIP4P)	2.8	2.5	2.5	2.2
CH$_3$OH	2.8	1.8	2.7	2.0
THF	2.8	2.0	2.7	2.0
MeOMe	2.9	1.9	2.7	2.0
	R_{i-C} (Å)	CN	R_{i-C} (Å)	CN
CH$_3$CN	4.0	2.8	3.9	2.6
	(R_{i-CH}) (Å)	CN	(R_{i-CH}) (Å)	CN
CHCl$_3$	4.8	2.0	4.8	2.4
	(R_{i-Cl}) (Å)	CN	(R_{i-Cl}) (Å)	CN
CCl$_4$	3.6	0.5	3.5	0.3
	R_{i-CH_2} (Å)	CN	R_{i-CH_2} (Å)	CN
CH$_2$Cl$_2$	4.9	2.9	4.8	2.8
C$_3$H$_8$	4.5	1.7	4.8	1.7

Comparing the stability constant ($\Delta \log K_s$) of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 in H$_2$O (TIP4P) and CH$_3$OH in this study with those in ref 32, those of H$_2$O (TIP4P) and CH$_3$OH in this study are 0.81 and 1.07, and those of H$_2$O and CH$_3$OH in ref 32 are 0.64 and 1.03, respectively. In contrast to them, the stability constant ($\Delta \log K_s$) of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 in the other solvents is also expected to be reliable.

3.4. Structural Properties and Radial Distribution Function (RDF). The solvent−complex ion structure can be characterized through RDFs, $g_{ai}(r)$, which give the probability of finding an atom of type i a distance r from an atom of type a.

The positions of the first maximum of the ion in the 18-crown-6 ion complexes (O, C, Cl, and CH$_2$) in the solvents obtained from RDFs are listed in Table 3. They decrease when the 18-crown-6/Rb$^+$ ion complex transforms to the 18-crown-6/K$^+$ ion complex in all solvents except CHCl$_3$ and C$_3$H$_8$. The coordination numbers (CN) of solvent molecules in the first coordination shell of 18-crown-6/Rb$^+$ ion and 18-crown-6/K$^+$ ion complexes evaluated by integrating ion (O, C, Cl, and CH$_2$) solvent RDFs to their first minimum are also listed in Table 3. The number of solvent molecules in the first coordination shell around the ion for all solvents except CH$_3$OH, THF, MEOME, CHCl$_3$, and C$_3$H$_8$ decreases when 18-crown-6/Rb$^+$ ion complex transforms to the 18-crown-6/K$^+$ ion complex.

In CH$_3$OH, THF, MEOME, CHCl$_3$, and C$_3$H$_8$, the number of solvent molecules in the first coordination shell of 18-crown-6/Rb$^+$ ion and 18-crown-6/K$^+$ ion complexes increases when 18-crown-6/Rb$^+$ ion complex transforms to the 18-crown-6/K$^+$ ion complex. Those trends could be explained by the strengthened and the weakened solvent−complex interactions when 18-crown-6/Rb$^+$ ion complex transforms to the 18-crown-6/K$^+$ ion complex.

Both the calculated and the experimental results are sensitive to the definition of CN. The hydration numbers of the

experimental are available from mobility measurements.[34] Those values correspond to the number of solvent molecules that have undergone some constant critical change due to the complex, a change that is susceptible to measurement by a particular experimental technique. Such hydration numbers are often quite different from CNs based on a structural definition, like those from diffraction experiments.[35] Mezei and Beveridge obtained their values by integrating the ion center of mass of water RDFs up to the minimum of the first peaks.[36]

These hydration numbers will not be significantly different if they are based on ion oxygen RDFs. This is a straightforward definition, and this has been adopted for all of the calculated values for 18-crown-6/Rb$^+$ ion and 18-crown-6/K$^+$ ion complexes.

The RDFs of 18-crown-6/Rb$^+$ ion and 18-crown-6/K$^+$ ion complexes in selected solvents for clarity are plotted in Figures 2 and 3. As shown in Figure 2, the ordering of smaller r value, the positions of the first maximum of the 18-crown-6/Rb$^+$ ion complex (O, Cl) in the solvents is THF = CH$_3$OH < H$_2$O (TIP3P) < CHCl$_3$ < CCl$_4$. However, the ordering of smaller r value, the positions of the first maximum of the 18-crown-6/K$^+$ ion complex (O, Cl) in the solvents is CH$_3$OH = THF < H$_2$O (TIP3P) < CHCl$_3$ < CCl$_4$, shown in Figure 3, and the $g(r)$ intensity of the first peak is changed as 18-crown-6/Rb$^+$ ion complex transforms to the 18-crown-6/K$^+$ ion complex. That is due to interaction changes between the 18-crown-6/Rb$^+$ ion or 18-crown-6/K$^+$ ion complex molecule and the solvent molecule, i.e., the CN changes of solvent molecules in the first coordination shell of 18-crown-6/Rb$^+$ ion and 18-crown-6/K$^+$ ion complexes.

In Figures 2 and 3, the second peaks are located between 6 and 8 Å in THF, CH$_3$OH, CHCl$_3$, CCl$_4$, and H$_2$O (TIP3P) solutions. In Figure 2, the second peaks of THF and CH$_3$OH have the bigger peak intensities than the others, which indicate that 18-crown-6/Rb$^+$ ion complex in THF and CH$_3$OH has the clear second solvation shell. Those could be explained by the fact that the relatively stronger complex molecule−solvent molecule interactions exist in THF and CH$_3$OH solutions than in the others. The strong complex molecule−solvent molecule interaction in THF and CH$_3$OH solutions is also due to the electron pair donor properties of the solvent molecule to ion in complex, i.e., DN.[33]

In Figure 3, the second peak of THF has also the bigger peak intensities than the others, which indicate that 18-crown-6/K$^+$ ion complex in THF has the clear second solvation shell. Those could also be explained by the fact that the relatively stronger complex molecule−solvent molecule interactions exist in THF solutions than in the others.

We could not compare the structural properties and radial distribution function data from this study with the published work because there were no studies for structural properties and radial distribution function when 18-crown-6/Rb$^+$ ion complex transforms to the 18-crown-6/K$^+$ ion complex in the organic solvents. From those trends, we have noted that the degree of the complex ion−solvents interactions is dependent on the Born's function of the solvents, the electron pair donor properties of the solvent, the radii of host and guest, and the differences in solvation.

4. Conclusion

The solvent effect on differences in stability constant ($\Delta \log K_s$) as well as the relative free energies of binding of Rb$^+$ and K$^+$ ion to 18-crown-6 have been studied by the Monte

Study of Solvent Effect on $\Delta\log K_s$
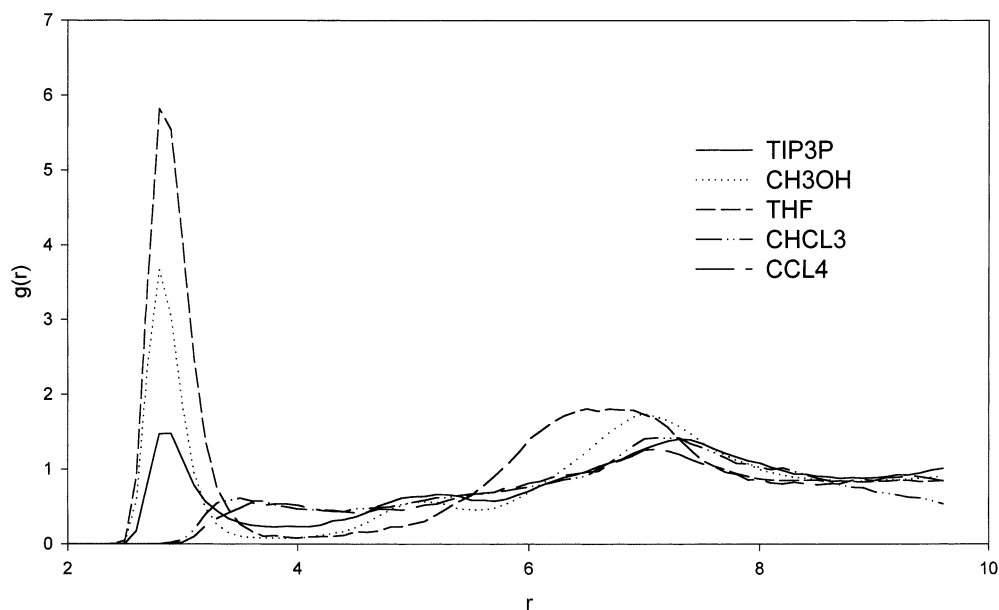
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Figure 2. Radial distribution function, $g(r)$, of 18-crown-6/Rb^+ ion complex in selected solvents. Distances are in angstroms throughout.
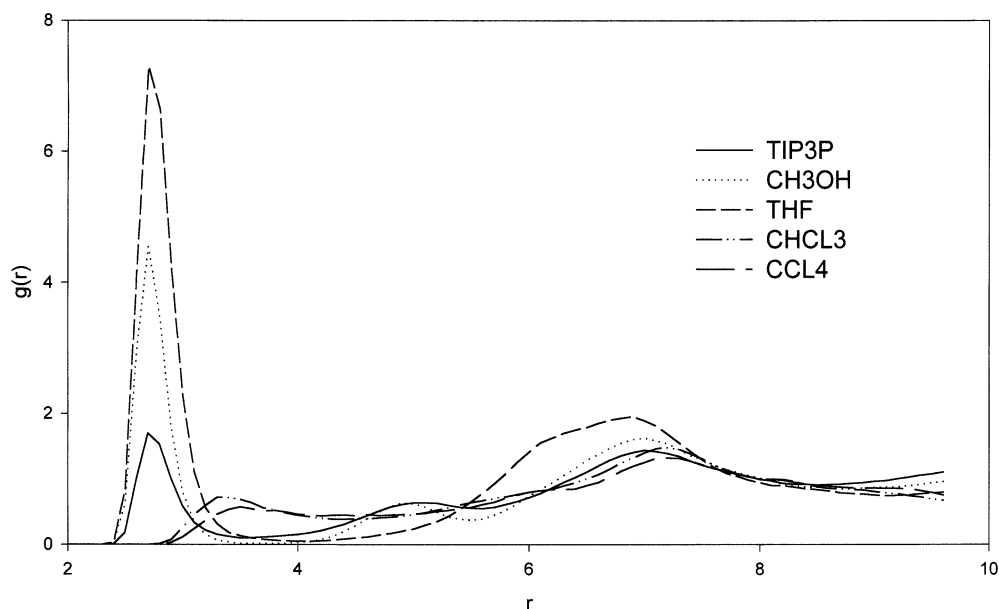

Figure 3. Radial distribution function of 18-crown-6/K^+ ion complex in selected solvents.

Carlo simulation of SPT, and we have compared differences in stability constant ($\Delta\log K_s$) as well as the relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6 in this study with those of the published works. There is good agreement among the studies if we consider both methods used to obtain the stability constant ($\Delta\log K_s$) of binding of Rb^+ and K^+ ion to 18-crown-6 and standard deviations. We also have studied for structural properties and radial distribution function when 18-crown-6/Rb^+ ion complex transforms to the 18-crown-6/K^+ ion complex. From this study, we noted that Born's function of the solvents, the electron pair donor properties of the solvent, the radii of host and guest, and the differences in solvation dominate the differences in the stability constant ($\Delta\log K_s$) as well as the relative free energies of binding of Rb^+ and K^+ ion to 18-crown-6. The results in this study obtained by the Monte Carlo simulation of SPT appear promising in providing estimates of the solvent effects on stability constant of ions binding to ionophores and similar species among polar solvents and the less polar or nonpolar solvents.

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