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Complex Formation between KI and Crown Ethers in Methanol, Ethanol and 1-Butanol at Different Temperatures

Abstract

Formation of complexes of Potassium Iodide with crown ethers was investigated in methanol; ethanol and 1-butanol at 308.15 and 313.15 K. Stability constants of the resulting complexes were estimated by means of calorimetric methods. The results obtained have been discussed in the light of formation of inclusion complexes between crown ether and other compounds.

Keywords: Crown ethers, Methanol, Ethanol, Calorimetry, host–guest complex, enthalpy of mixing, hydrophobic cavity.

Atri D. Tripathi[1]*
Souvik Sur[2]

Author Affiliations
[1]Dept. of Chemistry, Faculty of Engineering, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh 244001, India.
[2]Research and Development Center, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh 244001, India.

***Corresponding Author**
Atri D. Tripathi,
Dept. of Chemistry, Faculty of Engineering,
Teerthanker Mahaveer University, Moradabad,
Uttar Pradesh 244001, India.

E- mail: atri34tmu@gmail.com

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INTRODUCTION

An Inclusion compound is a complex compound in which one compound (the "host") has a pit into which "visitor" compound can be suited [1-4]. The collaboration between the host and visitor includes only Van der Waals bonding. The meaning of inclusive complexes is wide, reaching out to divert framed between molecules in the crystal lattice in which visitor atoms can fit. Crown ether is the instance of formation of these complexes, which we have studied in the present work.

CROWN ETHER

18-C-6 (Crown ether), additionally called as "crown compound" due to its shape just like crown, is taken as a class of those compounds which has a distinct property of completion and was discovered after 1969s. This is a macro-cyclic polyether which contains $[CH_2CH_2Y]_n$ (where n is greater than 2 units, in which Y is O or N or S or P (heteroatom). Crown ether refers to the macro-cyclic polyether, in such case Y is taken as Oxygen, for example 18-C-6 and dicyclohexyl-18-C-6. 18-C-6 has the formula $[C_2H_4O]_6$ and the IUPAC name of 1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane. S_6 is the point group of 18-crown-6 and its dipole moment varies in different solvent and under different temperature. These ethers are named for the order of the ring atom size and the non-ring substituent, the group name (crown) and the ring hetero atom quantity in accordance with the usual nomenclature.

Crown ether which are saturated, is a colorless, sticky or low-elastic stable liquid while a colorless crystal is aromatic ring-containing crown ether. Crown ethers which contains aromatic ring are extra soluble in dichloromethane, chloroform, pyridine and formic acid in water, alcohol and frequent natural solvents at ordinary temperature. Crown ethers containing cyclohexyl are more soluble in water, alcohols and fragrant hydrocarbons than the equivalent benzo-crown ether, plus in petroleum ether.

Crown ether has an exact thermal immovability. Its ether bonds are at risk to oxidation when melted. The molecule containing the aromatic ring can take phase when the process of nitration or, bromination or esterification or ozonization occurs, and structure a polymer with formaldehyde at the time of condensation. Crown ether has a property that it can shape a complex substance known as crypate exposé many salts soluble in non-polar organic solvent, thus tough reactions can be done without difficulty. The more appropriate the lipophilic is, the higher catalytic undertaking it possess.

The reaction is selective due to its constant cavity can only accommodate ion of the particular size. Ring and efficient ions; and the steadiness constant for this crypate is typically low once established with the help of electrostatic interactions. Its lipophilic aspect is more appropriate. Its catalytic activity is greater. Moreover, the reaction is selective, given that only ions of the respective size can be recognized by its permanent home. The stability of the formed by crown ethers and fantastic ions on the relative measurement of polyether is generally known. What makes the reaction convenient is, by adding water, the complexing can be broken down without problems by diluting the acid or heat decomposition [6-9].

Apparently, 18-C-6, dibenzo-18-C-6 and dicyclohexyl-18-C-6 are the most frequently used crown ethers accessible without problems. It is a main aspect of crown ethers to form complexes with metallic cations which are used in natural synthesis for segment transfer catalysis.

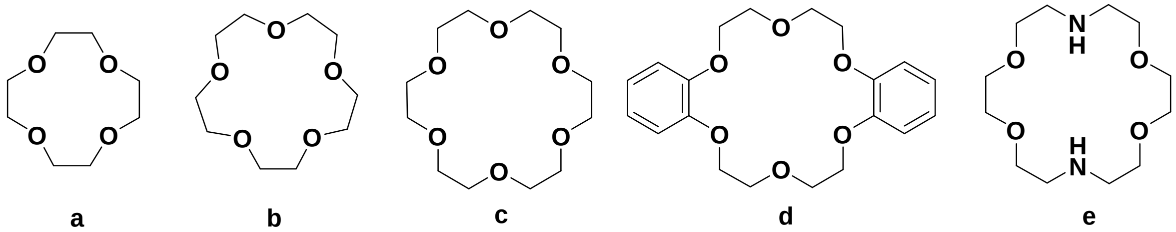

Figure 1: Structure of common crown ethers: a. 12-crown-4, b. 15-crown-5, c. 18-crown-6, d. dibenzo-18-crown-6 and e. diaza-18-crown-6.

Crown ethers have shown to be special cyclic molecules for the molecular identification by means of hydrogen-bondings, interactions between ions and interactions which are hydrophobic of suitable substrates. 18-Crown-6 has a high affinity for the hydronium ion H_3O^+, as it can fit inside the crown ether. Studying interactions involving complexing of various cations with crown ethers in solvent mixtures is important for a better perceptive of the many phenomenon like molecular recognition and different other analytical applications.

Across many ways Crown ethers have found applications based on their ability to selectively detect metal and ammonium ions. In analytical chemistry, their active metal ion binding properties are utilized for the recovery or removal of cations, their concentration from much diluted solutions and the design of ion-selective electrodes in separation and transportation processes. It is also used in chromatographic technique, due to its bonding to the stationary phase [10].

Thermodynamic studies allow a deeper perspective of the driving forces behind the relationships between the host and guest. In general, a cation-ligand complex is characterized by its geometric properties like its structure and conformation, as well as thermodynamic properties such as stability, enthalpy and complex formation entropy. The size of the crown ether and the number of donor atoms depend on the stability and selectivity of the crown ether complexes. This also plays a main component in the continued existence of ligand and cation [11]. It is observed that the macro cyclic ligands 'intramolecular cavity size' very much effects the complex's stability constant (the chosen cation is the one that better accommodates into the cavity). Thus cation and cavity diameter of crown ether have also been used as parameters for predicting about selectivity and formation of complexes. Crown ether (18-C-6) is a synthetic molecule whose features have constituted an important field of investigation over the last few decades. Many applications in chemistry and biochemistry is due to its selective affinity and binding with metal ions in solutions. Although the complexation reaction between the macrocyclic ligands and the metal ion in a given medium often includes rivalry between the cation and the ligand solvent, the "cavity selectivity law" that encompasses many primary effects (i.e. electrostatic ion-ligand interactions, van der waal powers, ligand conformational shifts, enthalpy /entropy inputs) does not occur in wheeled structures.

In this paper we report the complexing capacity of crown ether (18-C-6) at different temperatures using calorimetric method with potassium iodide in methanol, ethanol, and butanol.

EXPERIMENTATION

The 18-crown-6 macrocyclic ligand (from Merck) was extracted from acetonitrile and vacuum dried. Methanol, ethanol, and butanol (All chemicals are of AR quality, BDH 99.59 mol% pure) were activated over molecular sieves 4A^0 before use. Potassium iodide (Ranbaxy Laboratories Ltd, high pure) used without further purification.

PROCEDURE

Experiments were conducted on C-80 microcalorimeter by batch method [7,8], the calorimeter consists of a reference vessel and an experimental one. They are surrounded by two symmetrical Thermal flux meter consisting of sequence thermocouples. The entire assembly is held in an aluminum block and the thermal equilibrium can be achieved. If there is any heat released or absorbed in the experimental vessel, this will result in temperature changes being allowed and this will persist until the same temperature in both vessels is reached. The experimental cell has two separate chambers with a tilting lid. The samples are inserted separately by equilibrium into the tank. The mixing happens by inverting the entire calorimeter by 180^{0}C. By determining the region under the curve obtained during the experiment, the amount of heat, q developed during an experiment can be determined. The concentration of 18-C-6 over the entire experiment was 0.1 M and 0.05 M for potassium iodide.

Calculation of K and ∆H

If the initial concentrations of KI and crown ether are a_0 and b_0 respectively and V_1 and V_2 are their volume then the concentrations of crown ether, b and that of KI , a, in the solution are given by

$$a = \frac{a_0 V_1}{v_1+v_2} = \frac{a_0 v_1}{V}$$
$$b = \frac{b_0 v_2}{v_1+V_2} = \frac{b_0 v_2}{V}$$

And we have

$$\frac{x}{(a-x)(b-x)} = K$$

Where x is the concentration of the inclusion complex and K is the stability constant for the reaction.

If one of the reactants has much higher concentration than other than some simplification can be introduced. For example if a<<b then

$$\frac{x}{(a-x)} = bK$$

Or

$$x = \frac{abK}{(1+bK)}$$

Now ΔH_0 and q (q is the heat evolved) are related by the equation

$$q = \frac{\Delta \text{H0}\ x(v1+v2)}{1000} = \frac{\Delta \text{H0}\ (v1+v2)}{1000}\ \frac{Kab}{1+bK}$$

$$\frac{1}{\Delta \text{H}} = \frac{1}{\Delta \text{H0}} + \frac{bv2}{\text{H0}\ K(v1+v2)}$$

Δ H= $\frac{1000q.}{\text{av1}}\frac{(v1+v2)}{\text{bv2}}$ =standard molar enthalpy of inclusion.

Now if we plot the experimental quantities $\frac{1}{\Delta \text{H}}$ agains t$\frac{bv2}{(\text{v1+v2})}$, then slope will be $\frac{1}{\Delta \text{H0}}$ whereas intercept, $\frac{1}{k\Delta H_0}$.

Thus K= $\frac{slope}{\text{intercept}}$

RESULTS AND DISCUSSION

The values of mass m1 and m2, volume, v1 and v2 for different compounds, q, and ΔH have been collected in Table 1 to Table 4, for the complexation of crown ether with KI in different solvents i.e.CH_3OH, C_2H_5OH and butanol at different temperatures. The values of stability constants or equilibrium constants, K of crown ether with different solvents, the intercept, $\frac{1}{K\Delta H}$, and the slope $\frac{1}{\Delta H}$ at different temperatures have also been collected at different temperatures in Table 5. The values of $\frac{bv2}{(\text{v1+v2})}$ against $\frac{1}{\Delta \text{H}}$ for butanol system have been plotted in Figure 2.

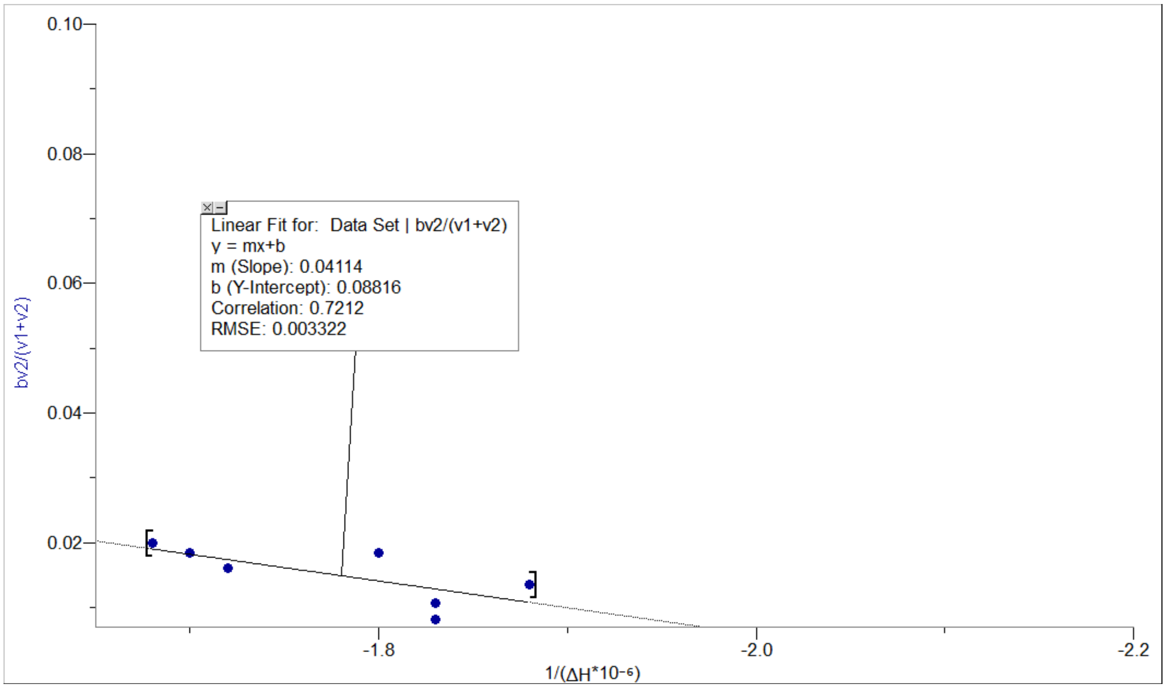

Figure 2: Plot of $\frac{1}{\Delta \text{H}}$ against $\frac{bv2}{(\text{v1+v2})}$ for the system (KI +18C6) in 1-butanol at 35^0 C

The values of equilibrium constant are high because of the complex formation between the guest, K^+, and the host, 18-C-6. The cavity radius of 18-crown-6 is 1.34 to 1.43 A^0 [12], while the ionic radii of K^+ 1.38A^0. Thus the size matching may allow the host to reorganize and desolvate for complexing act [13]. Crown ethers have a strong alkaline and alkaline earth metal ions affinity due to its size which accommodates into the cavity.

Table 1: Various parameters for the system (KI +18C6) in methanol at 35^0 C (a_0=0.05, b=0.1)

m1 (g)	m2(g)	v1(cc)	v2 (cc)	q*10^{-3}	m2v2	v1+v2	bv2/v1+v2	ΔH(J)
2.1900	0.4013	2.8185	0.5165	-1130.4	0.20727	3.335	0.0155	-517935
1.7074	0.4035	2.1974	0.5193	-1114.98	0.2095375	2.7167	0.0191	-530900
1.2469	0.4052	1.6048	0.5215	-1145.85	0.211312	2.1263	0.0245	-582247
2.5260	0.4443	3.251	0.5718	-1350.33	0.2541	3.8228	0.01496	-555380
2.8559	0.4299	3.6755	0.5533	-1224.85	0.2379	4.2288	0.013084	-509393
2.5930	0.4628	3.3372	0.5956	-1302.01	0.2756	3.9328	0.0151	-515239
2.6645	0.4210	3.4292	0.5418	-1147.7	0.22809	3.971	0.0136	- 490599

Table 2: Various parameters for the system (KI +18C6) in methanol at 40^0 C (a_0=0.05, b=0.1)

m1 (g)	m2(g)	v1(cc)	v2 (cc)	q*10^{-3}	m2v2	v1+v2	bv2/v1+v2	ΔH(J)
1.8549	0.4246	2.4012	0.5496	-1104.6	0.2334	2.9508	0.018626	- 493984
1.4011	0.3951	1.8137	0.5115	-931.73	0.2021	2.3252	0.0220	-467056
1.3100	0.5030	1.6958	0.6511	-1488.9	0.3275033	2.3469	0.0277	-632926
2.1274	0.3812	2.7539	0.4935	-1248.7	0.18812	3.2474	0.01519	-596749
1.3313	0.5021	1.7234	0.6500	-1508.06	0.3264	2.3734	0.0274	-639028
1.4301	0.5012	1.8513	0.6488	-1501.4	0.2456	2.5001	0.0260	- 625023

Table 3: Various parameters for (KI +18C6) in ethanol at 35^0 C (a_0=0.05, b=0.1)

m1(g)	m2(g)	v1(cc)	v2 (cc)	q*10^{-3}	m2v2	v1+v2	$\frac{bv2}{v1+v2}$	ΔH(J)	$\frac{1}{\Delta H * 10^{-6}}$
2.5897	0.5132	3.3342	0.6607	-2056.4	0.3391	3.9949	0.0165	-745870	-1.341
2.0423	0.4844	2.62945	0.6301	-2013.9	0.3084	3.2596	0.0193	-792428	-1.262
1.9190	0.4721	2.4707	0.6078	-1944.5	0.2870	3.0785	0.0197	-797238	-1.254
2.0569	0.4912	2.648	0.6324	-2010	0.3106	3.2807	0.0193	-787505	-1.27
2.5314	0.5260	3.259	0.6772	-2044.8	0.3562	3.9364	0.0172	-729377	-1.37
1.9257	0.4702	2.479	0.6054	-1952.2	0.2847	3.0847	0.0196	-802392	-1.246
1.9328	0.4753	2.4885	0.6119	-1932.9	0.2909	3.1004	0.0197	-787123	-1.27

Table 4: Various parameters for (KI +18C6) in 1-butnol at 35^0 C (a_0=0.05, b=0.1)

m1(g)	m2(g)	v1(cc)	v2 (cc)	q*10^{-3}	m2v2	v1+v2	$\frac{bv2}{v1+v2}$	ΔH(J)	$\frac{1}{\Delta H * 10^{-6}}$
2.0844	0.4692	2.6116	0.5879	-1334.9	0.2758	3.1995	0.0184	-556353	-1.8
2.0047	0.4509	2.5117	0.5649	-1377.3	0.2547	3.0766	0.0184	-597297	-1.7
1.7500	0.4339	2.1926	0.5436	-1296.3	0.2359	2.7362	0.0199	-595174	-1.68
2.3620	0.4533	2.9594	0.5680	-1385.05	0.2575	3.5274	0.0161	-581297	-1.72
3.7048	0.4434	4.6419	0.5555	-1359.97	0.2463	5.1974	0.0107	-548234	-1.83
4.8881	0.4388	6.1244	0.5498	-1379.3	0.2412	6.6742	0.0082	-546773	-1.83
3.2035	0.5023	4.0138	0.6293	-1447	0.3161	4.6431	0.0136	-531896	-1.88

Table 5: Values of ΔH and Equilibrium constant, K at different temperatures for various systems

System	T(K)	Intercept, $\frac{1}{K\Delta H}$	Slope, $\frac{1}{\Delta H}$	ΔH(kJ)	Equilibrium constant, K
(KI+18C6) in Methanol	308.15	2.22X10^{-6}	0.187X10^{-4}	-52.1	8.41
	313.15	2.22X10^{-6}	0.187X10^{-4}	-53.6	8.89
(KI+18C6) in Ethanol	308.15	1.8X10^{-6}	0.187X10^{-4}	-58.1	10.6
(KI+18C6) in Butanol	308.15	1.94X10^{-6}	0.13X10^{-4}	-77	4.6

The main factor which controls the attractive (bonding) force and selectivity is the capability of the size between the cation present and the cavity of the ligand. The cations that better suit the cavity are in the middle and maximize the interactions with the oxygen (heteroatom). The maximum selectivities are said when radius ratios are about 1.0.

The bonding of alkali ion with the Oxygen is purely electrostatic. In this case the charge density given by cation is prevailing. Solvation of species concerned in the complex formation also plays an essential role. For solvent interactions, both host and guest participate. The relationships between cation / ligand compete against the liberation of cations.

From the results we can see that in the case of ethanol system the value of the stability constant is more in comparison to methanol and butanol. The reason behind it seems to be that ethanol is more polar i.e. has more electron donating property than methanol, and 1-butanol. The electrostatic nature of the bonding between the oxygen atoms and cation and the stronger solvation of potassium ion in ethanol lead to a larger stability of complexes in ethanol.

CONCLUSION

From the results obtained from careful experiments above, it has been concluded that the values of stability constant is high in case of crown ether-ethanol complexation. The complex formed is inclusion complexes and the stronger solvation of potassium ion in ethanol results in the formation of strong complex.

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