Original Article

Bulletin of Pure and Applied Sciences.
Vol.37 C (Chemistry), No.2, 2018: P.163-170
Print version ISSN 0970 4620
Online version ISSN 2320 320X
DOI 10.5958/2320-320X.2018.00024.9

Thermodynamics of Inclusion Complexes in Water α-cyclodextrin – Alkyl Halides Adducts at 303.15, 308.15 and 313.15 K

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Received on 5th February 2018
Accepted on 31th March 2018

Abstract

The interaction in water of tetra ethyl ammonium bromide($(C_2H_5)_4N(Br)$), tetra propyl ammonium bromide ($(CH_3CH_2CH_2)_4N(Br)$)and tetra butyl ammonium bromide ($(CH_3CH_2CH_2CH_2)_4N(Br)$) with α-cyclodextrin (α-CD, cyclohexaamylose) ($C_{36}H_{60}O_{30}$) has been studied calorimetrically at the temperature 303.15 , 308.15 and 313.15 K. The values of enthalpy of mixing, Q of two binary aqueous solutions of α-CD with alkyl halides at all temperatures have been fitted by the method of least squares to the equation $Q = x_1x_2[Ao + A_1(x_2 - x_1) + A_2(x_2 - x_1)^2]$, where x_2 refers to the mole fraction of the alkyl halide . The results obtained have been interpreted.

Keywords: Microcalorimeter, α-cyclodextrin, tetra ethyl ammonium bromide, aqueous solutions, enthalpy of mixing.

1. INTRODUCTION

Cyclodextrins (CDs) are cyclic oligomers of glucopyranose units which form inclusion complexes with many organic substances. These interactions are non-covalent. Their uses in the study of supramolecular chemistry are well known. Due to its biocompatibility and non-toxicity CDs have been widely applied for encapsulation of different substances, being used in biological, cosmetic and pharmaceutical fields [1, 2].

To understand the forces involved in the specific interactions of α-CD ($C_{36}H_{60}O_{30}$) with some nonelectrolytes in aqueous solutions, it is observed that mixing experiments are widely used to collect information on the thermodynamic parameters characterizing that process. α-CD is mainly hydrophilic in character at the outside of the cavity but at the inside, it is hydrophobic . They possess a hydrophobic cavity which makes them suitable for the formation of inclusion complexes. The α-CD contains 18 hydroxyl groups, which can be modified chemically. The most notable feature of cyclodextrins is their ability to form solid inclusion complexes (host–guest complexes) with a very wide range of solid, liquid and gaseous compounds by a molecular complexation . In these complexes, a guest molecule is held within the cavity of the cyclodextrin host molecule. Complex formation is a dimensional fit between host cavity and guest molecule.

The lipophilic cavity of cyclodextrin molecules provides a microenvironment into which appropriately sized non-polar moieties can enter to form inclusion complexes. No covalent bonds are broken or formed during formation of the inclusion complex. In the present program, the interaction between α-CD with tetraethyl ammonium bromide(TEAB), tetrapropyl ammonium bromide(TPAB) and tetra butyl ammonium bromide

(TBAB)with α-cyclodextrin (α-CD, cyclohexaamylose) have been undertaken calorimetrically at 303.15,308.15 and 313.15 K. This approach permits one to evaluate the enthalpic effect connected with the inclusion process, Q. The results obtained have been reported and interpreted in this paper.

2. EXPERIMENTAL

α-CD was a crystalline sigma product. Tetraethyl ammonium bromide (TEAB), tetra propyl ammonium bromide (TPAB) and tetra butyl ammonium bromide (TBAB) (All Fluka products) were of the highest purity commercially available and were used without further purification. Chromatographic analysis showed no organic impurities and the water content did not exceed 0.01%. All compounds were activated over molecular sieve $4A^0$ before use.

Calorimetric measurements were carried out using micro calorimeter (Setaram C-80 model) at 303.15 308.15 and 313.15 K.

Experiments have been done by batch method on C-80 calorimeter [3]; the calorimeter consists of a reference and experimental vessel. These are surrounded by two symmetrical thermal flux meters composed of thermocouples in series. The whole assembly is kept in an aluminum block and allowed to reach thermal equilibrium. If there is any heat liberated or absorbed in the experimental vessel during mixing of α-cyclodextrin and alkyl halide, it leads to change in temperature which is allowed and this persists till same temperature is attained in both the vessels. The experimental cell has two chambers separated by tilting lid. The samples are separately introduced into the vessel. The mixing is performed by inverting the whole calorimeter by 180^0C. The amount of heat, q evolved during an experiment can be calculated by determining the area under the curve obtained during the experiment. The concentration of the concentration of α-cyclodextrin was 0.1M and 0.5M for alkyl halide throughout the experiment. The heat of dilution of the guest was measured separately, for which appropriate corrections were made throughout the work using following relation:

$$Amount\ of\ heat\ (experimental) = \\ q1(heats\ of\ dilution\ of\ alkyl\ halide) + q2(heats\ of\ dilution\ of\ \alpha - \text{cyclodextrin}\ ) + \\ \text{q(of inclusion complex)}$$

3. RESULTS AND DISCUSSION

If the initial concentrations of α-cyclodextrin and alkyl halide are $a0$ and $b0$ respectively and $v1$ and $v2$ are their volumes and the heat evolved denoted by q , then mole fraction of α-cyclodextrin, $x1$ is given by

$$\boldsymbol{x1} = \frac{\boldsymbol{a0v1}}{\boldsymbol{a0v1+bov2}}\boldsymbol{v} \qquad (1)$$

$$\text{and } \boldsymbol{x2} = \boldsymbol{1 - x1} \qquad (2)$$

Enthalpy of reaction, Q, is given by

$$\boldsymbol{10Q} = \frac{qx10^3}{a0v1+b0v2}$$

The values of $\boldsymbol{Q}$, obtained in the present investigation for the mixtures of {x1 α-cyclodextrin +x2 TEAB}, {x1 α-cyclodextrin +x2 TPAB}and {x1 α-cyclodextrin +x2 TBAB} at the temperature 303.15, 308.15 and 313.15 K have been given in the Table1. The values of Q for the various mixtures have been fitted by the method of least-squares to the Redlich–Kister type equation**:**

$$Q\ (\text{J.mol}^{-1}) = x_1x_2[A_o + A_1(x_2 - x_1) + A_2(x_2 - x_1)^2] \qquad (3)$$

The resulting values of the coefficients A_0, $A_1$and A_2 of Eq. (3), and the standard deviations δ (Q) of the fits for the different mixtures are given in Table 2. Graphical presentation of experimental values of data is presented in Figure1.The precision in the values of Q is of the order of±0.5 J.mol^{-1}. The present Q values are observed to be positive throughout the entire range of x_2 for the mixtures of {x_1 α-cyclodextrin +x_2 TEAB}, whereas negative for binary mixtures of {x_1 α-cyclodextrin +x_2 TPAB} or {x_1 α-cyclodextrin +x_2 TBAB}.

It clearly suggests that interaction become stronger with increasing length of alkyl chain. The structure of α-cyclodextrin in water is similar with the α-cyclodextrin hexahydrate in the crystalline state [4,5]. The void molecule of α-cyclodextrin has two water molecules entrapped in the cavity, which are hydrogen bonded to each other and to two hydroxyl groups of the glucopyranose rings. The formation of a complex implies, at first, that these water molecules are squeezed out on relaxing to the bulk, and then the alkyl bromide (guest) molecule can enter the cavity. The interaction between host and guest molecule must be weak and only dispersion and vander waal's forces are operative in such type of interaction. Due to this, the smaller molecules are disordered at the interior of the cavity; this is in accordance with our results that the values of Q are positive for the system of $C_{36}H_{60}O_{30}$ + TEAB at both the temperatures. The fitting to the cavity improves as the dimension of the guest molecule increase, thus showing higher negative values of Q in the case of the system of α-cyclodextrin + TPAB or TBAB , which clearly indicates that there is a strong complex formation between these two components. The higher negative values of Q in the case of the system of α-cyclodextrin + TBAB at all temperatures shows that the TBAB molecules are strongly fitted to the cavity and strong inclusion complexes are formed. Further at all temperatures, the values of Q decrease in the order

TEAB> TPAB> TBAB

This behavior clearly indicate presence of weak forces involved with α-cyclodextrin + TEAB system due to hydrophobic interaction, whereas strong bond formation is indicated with α-cyclodextrin + TPAB or TBAB. As the value of negativity is more with TBAB, it suggests that the bond between α-cyclodextrin + TBAB is stronger than α-cyclodextrin -TPAB system. The main driving force of complex formation is the release of enthalpy-rich water molecules from the cavity. Water molecules are displaced by more hydrophobic guest molecules present in the solution to attain an apolar–apolar association and decrease of cyclodextrin ring strain resulting in a more stable lower energy state. The sign of Q, positive or negative for above mentioned systems suggests that for α-cyclodextrin complexes, the hydrophobic interactions do not always play the major role in the formation of these inclusion complexes. Dipole-induced dipole, host-guest interactions and the decrease in the activation energy when a hydrophobic residue fills the cavity must also be considered as important effects. The positive value indicates that the formation of complexes implies squeezing out water molecules entrapped in the cavity, and then the guest molecule can penetrate the cavity with a modification of the solvent in its hydration cosphere. The negative values of Q are the result of all types of interactions involved.

Table 1: Enthalpies of mixing (Q) of ($C_{36}H_{60}O_{30}$) (1) + TEAB (2), or + TPAB (2), or + TBAB (2), at 303.15, 308.15 & 313.15 K.

α-cyclodextrin + TEAB at 303.15K	
$x2$	$Q(J.mol^{-1})$
0.9663	18
0.9643	19
0.9422	26
0.9303	32
0.9124	38
0.9091	39
0.8893	43
0.8435	52
0.8206	54
0.8111	56
0.7644	60
0.7555	61
0.7236	62
0.7003	65
0.6846	65
0.6513	67
0.6417	68
0.6352	70
0.5738	79

α-cyclodextrin + TEAB at 308.15K	
$x2$	$Q(J.mol^{-1})$
0.9916	**4**
0.9789	**9**
0.9645	**14**
0.9535	18
0.9428	23
0.9346	26
0.9127	27
0.8944	38
0.8811	41
0.8766	43
0.8444	52
0.8002	62
0.7887	64
0.7442	68
0.7328	71
0.7113	73
0.6767	77
0.6045	83
0.5025	79

0.4568	101
0.3544	123
0.2357	136
0.1544	123
0.0458	55

0.4328	76
0.2568	61
0.1175	33
0.0633	21

α-cyclodextrin + TEAB at 313.15K	
$x2$	$Q(J.mol^{-1})$
0.9289	38
0.912	44
0.9044	47
0.8994	48
0.8766	55
0.8544	61
0.8322	63
0.8111	70
0.7593	78
0.7322	81
0.7137	84
0.6888	85
0.6544	92
0.6331	95
0.5433	99
0.4322	130
0.3124	151
0.2432	158
0.1035	111
0.0666	79

α-cyclodextrin + TPAB at 303.15K	
$x2$	$Q(J.mol^{-1})$
0.9555	-19
0.0557	-23
0.0667	-27
0.0876	-35
0.0951	-36
0.1035	-38
0.1123	-41
0.1345	-46
0.1567	-51
0.1787	-55
0.194	-57
0.2362	-60
0.2587	-64
0.2877	-65
0.3328	-68
0.4138	-66
0.4441	-65
0.4734	-64
0.5872	-59
0.6433	-55
0.7237	-48
0.8897	-25
0.9123	-21

α-cyclodextrin + TPAB at 308.15K	
$x2$	$Q(J.mol^{-1})$
0.9777	-15
0.9678	-22
0.967	-23
0.9632	-24
0.9503	-31
0.9358	-34
0.9232	-40

α-cyclodextrin + TPAB at 313.15K	
$x2$	$Q(J.mol^{-1})$
0.9875	-9
0.9677	-21
0.9544	-28
0.9345	-38
0.9488	-31
0.9211	-41
0.9014	-46

0.9022	-43
0.8877	-46
0.8644	-49
0.8594	-49
0.8413	-51
0.8234	-51
0.8021	-52
0.7355	-54
0.7013	-58
0.6433	-68
0.616	-76
0.606	-79
0.5411	-112
0.4589	-155
0.311	-250
0.2135	-279
0.1357	-250
0.0779	-181
0.0555	-141
0.0332	-92

0.8777	-50
0.8446	-53
0.8333	-53
0.8207	-54
0.7868	-52
0.7545	-51
0.7336	-49
0.7033	-46
0.6844	-45
0.6196	-42
0.5345	-47
0.4177	-71
0.3377	-92
0.2311	-115
0.1676	-109
0.0265	-34
0.0133	-18

α-cyclodextrin + TBAB **at 303.15K**	
$x2$	$Q(J.mol^{-1})$
0.9771	-73
0.9655	-105
0.9433	-159
0.9294	-190
0.9053	-234
0.8877	-254
0.8733	-274
0.8544	-290
0.8405	-305
0.791	-335
0.7766	-341
0.7544	-347
0.7273	-352
0.7024	-356
0.6734	-360
0.6283	-366
0.5511	-384
0.4438	-430

α-cyclodextrin + TBAB at 308.15K	
$x2$	$Q(J.mol^{-1})$
0.9869	-45
0.9669	-105
0.9568	-136
0.9325	-180
0.9211	-209
0.9014	-242
0.8893	-259
0.8655	-287
0.8433	-308
0.8214	-324
0.8111	-330
0.7981	-337
0.7766	-346
0.7464	-357
0.7322	-362
0.7194	-365
0.6713	-381
0.6212	-401
0.5791	-425

0.3644	-474
0.2112	-502
0.1118	-389
0.0778	-307
0.0322	-149

0.4667	-520
0.3322	-658
0.2466	-705
0.1174	-562
0.0656	-381
0.0323	-211
0.0113	-80

α-cyclodextrin + TBAB at 313.15K	
$x2$	$Q(J.mol^{-1})$
0.9844	-50
0.9777	-70
0.9655	-106
0.9533	-147
0.9211	-223
0.9107	-247
0.8766	-318
0.8666	-337
0.864	-342
0.8522	-363
0.8333	-393
0.787	-453
0.7752	-465
0.7054	-514
0.6891	-521
0.5757	-515
0.4556	-437
0.3334	-311
0.2135	-174
0.1445	-102
0.0433	-21

Table 2: Least Squares Coefficients of Eq 1 for the Enthalpies of mixing, and the standard deviations, σ, of α-cyclodextrin + TEAB, + TPAB, and + TBAB at 303.15, 308.15 and 313.15 K

System	**A$_0$**	**A$_1$**	**A$_2$**	**A$_2$** **σ/ (J mol^{-1})**
T=303.15K				
α-cyclodextrin (1) + TEAB (2)	364.5	401.5	638.9	0.8
α-cyclodextrin (1) + TPAB (2)	253.6	95.6	-135.6	0.7
α-cyclodextrin (1) + TBAB (2)	-1611	866.8	-2710	1.3
T=308.15K				
α-cyclodextrin (1) + TEAB (2)	323.5	-50.48	63.63	1.7
α-cyclodextrin (1) + TPAB (2)	- 520.7	1176	-1422	1.2
α-cyclodextrin (1) + TBAB (2)	-1950	1858	-3507	1.8
T=313.15K				
α-cyclodextrin (1) + TEAB (2)	460.7	-412.7	643.5	2.5
α-cyclodextrin (1) + TPAB (2)	-209.7	320.6	873.8	1.3
α-cyclodextrin (1) + TBAB (2)	-1889	1452	69.1	1.6

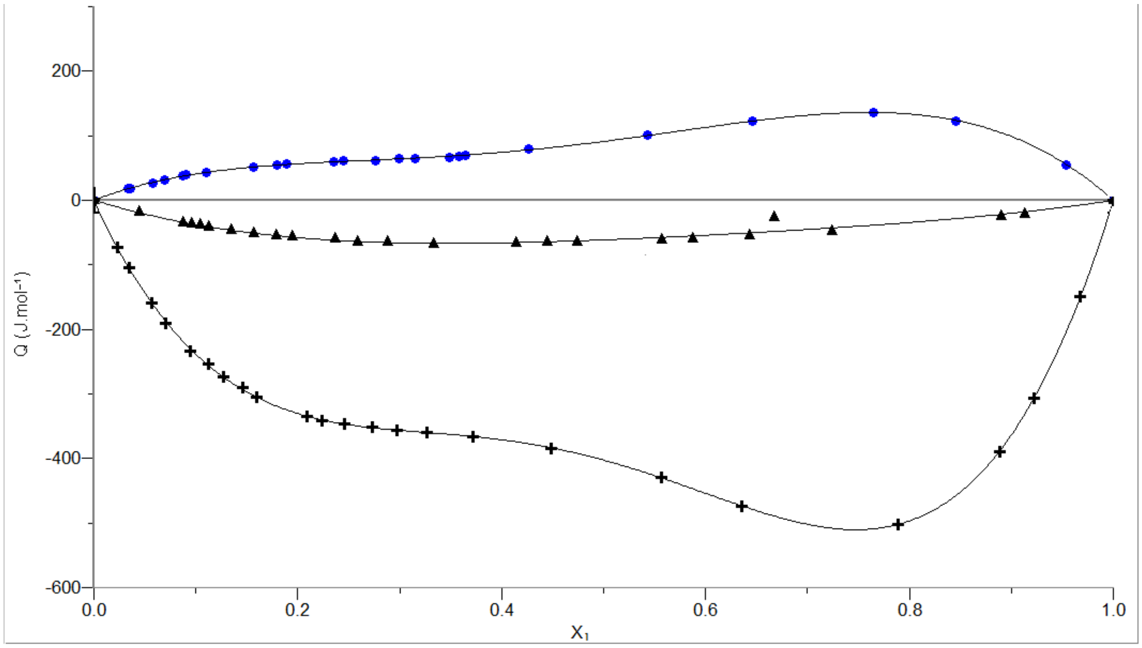

Fig.1: Enthalpies of solutions (Q) of aqueous binary liquid mixtures of x_1 of $(C_{36}H_{60}O_{30}$ $_2$(1) + ($((C_2H_5)_4N(Br))$ (●) (2), + $((CH_3CH_2CH_2)_4N(Br))$ ▲) (2), and + $((CH_3CH_2CH_2CH_2)_4N(Br))$(2) (✚) at 303.15 K, ——, calculated from equation (1).

4. ACKNOWLEDGMENT

Author is extremely grateful to Emeritus Professor D.V.S. Jain, Department of Chemistry, Panjab University, Chandigarh (India) for helping in various calculations and encouragement during course of present investigation.

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