Thermodynamic and Polarization Parameters of Dibenzo-18- crown- 6 in Mixed Methanol Water Solvents

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Abstract The different thermodynamic parameters for the solvation (Free energies, enthalpies, and entropies) (ΔG_s, ΔH_s &$T\Delta S_s$) for dibenzo–18–crown–6 in mixed methanol–water solvents were calculated form the experimental solubility data at different temperatures. From the experimental refractive indices and densities for the saturated solutions, the total polarization (P_t), polarizability (α), induced dipole moment (μ) and the contribution of the electronic permittivity (ε_∞) were evaluated. The solvation behavior of the crown ether used in these media was discussed in view of the estimated refraction and polarization parameters.Since dibenzo 18-crown-6 has a wide applications in analytical, industrial and biological ones, then the aim of this study is to explain its solvation behaviours in methanol.

Keywords Crown Ether, Solvation, Thermodynamic Parameters, Polarization, Mixed Methanol Water Solvents

1. Intoduction

In recent years, macrocyclic ligands have been used in ion chromatography as components of both the stationary and mobile phases. The interest in these molecules derives from their selectivity in binding specificcations. Some labs focused on the use of macro-cycles in ion chromatography in the separation of both cations and anions .Nakagawa et al. investigated the use of crown ethers in the mobile phase for the separation of amine cations, peptides, and sulfonic acids. They showed that the increase in capacity factors is related to the stability of the complex for those compounds that form complexes with the crown ether. They also showed that the concentration of crown ether influences the capacity factors for some compounds. Peak resolution between mono- and divalent cations using an unmodified silica gel column . The improved resolution is due to adsorption of 18-crown-6 onto the stationary phase and the formation ofmacrocycle-cation complexes with selected metal ions . The log*K* values indicate those metal ions that bind 18-crown-6 preferentially .Recently, Dionex developed the Ion Pac CS15 analyticalcolumn, which like its precursor the CS12A,contains phosphonate and carboxylate functionalgroups, but in addition contains 18-crown-6 groups[1-5].

Macrocyclic polyethers (crown ethers) are a family of compounds which possess the ability to transport ionic species across natural and artificial membranes. Because of this characteristic, they have wide applications in industry and

are being investigated for their potential as pharmacologic agents.However, these compounds are highly cytotoxic in both prokaryotes and eukaryotes. Because of the cytotoxicity of crown ethers, an investigation of the potential genotoxicity of these compounds in *Salmonella typhimurium* was used[6].

Crown ethers are very important, especially in application in thermodynamic studies[7], solvent extraction of divalent and monovalent ions[8], selective synergistic solvent extraction[9] and competitive complexation of some alkaline earths and transition metal ions[10]. Synthesis, characterization, crystal structure if some salts with dibenzo–18–crown– 6 and dibenzo–24–crown–8 macromolecules[11] are valuable ones. Therefore, studying the physical properties of the crown ethers, especially dibenzo–18–crown–6 are wanted to follow their behaviour in solutions like, apparent molar volumes and adiabatic compressibility[12].

The aim of this work is to evaluate the solvation, thermodynamic and polarization parameters of dibenzo–18–crown–6 in mixed methanol–water solvents at different temperatures.

2. Experimental

Dibenzo–18–crown–6 (DB18C6) was supplied from Merck. Methanol of BDH was used. Saturated solutions of DB18C6 were prepared by shaking 10 ml of different percentages of methanol and water in 15 ml glass tubes containing excess of the solid substance in a thermostatic water bath of the type Assistant 3193 at time intervals for a period of 2–3 weeks at 25, 30, 35 and 40°C. The molal solubility's of DB18C6 were measured (gravimetrically) by drying 1 ml of

the saturated solutions in small aluminium dishes or small beakers under a tungsten lamp to avoid scattering of the solutions as explained by Gomaa[13,14] .

The molal solubilities of DB18C6 in mixed MeOH–H_2O solvents were also confirmed by spectrophotometric measurements using (Unicom UV2–100 UV/ visible spectrometer V 3.32) by dissolving the above residues after evaporation in pure methanol and measuring the absorption at wave length (λ) of 275 nm done using different concentrations of DB18C6 in methanol mixture at the same wave length, small differences were observed in both measurements, there for the mean values were listed in Table 1.

The solubilities were read by the use from the standard curve. The refractive indices of the saturated solutions of DB18C6 were measured at 25, 30, 35 and 40℃ using a refractometer ATAGO 3T No.52507, 1 ml weighing bottle was used for measuring the densities of the saturated DB18C6 in mixed MeOH–H_2O solvents at different temperatures which used for calculating the molar volume by dividing the molecular weight by density values. The heat of evaporation for solid DB18C6 was done by using DSC (Differential Scanning Calorimeter) apparatus of the type Mettler TA 3000, DSC25, made in Switzerland.

3. Results and Discussion

The molal solubilities of DB18C6 were determined as reported in the experimental part at 25, 30, 35 and 40℃ in MeOH–H_2O mixtures with energy of ±0.001 g/L. Their solubility are shown in Table(1) which recorded from the average of minimum experiments with experimental error of ± 0.01

The solvation free energies for neutral compounds like tetraphenyl methane (Ph_4C), tetra phenyl germanium (Ph_4Ge)[8,9] DB18C6 in mixed MeOH–H_2O solvents were calculated from the molal solubility[10] by using the following equation (1):

$$\Delta G_s = -2.303 \ RT \log C \qquad (1)$$

Where C is the molal solubility of the crown ether used.

The transfer free energies for DB18C6 from water to mixed MeOH–H_2O solvents were calculated by applying equation (2) without correcting the activity coefficient[15].

$$\Delta G_t = -2.303 \ (\log C_{solvent} - \log C_{H2O}) \qquad (2)$$

Table 1. The solubility products of dibenzo –18 –crown 6 (DB18C6) in mixed methanol – water mixtures at different temperatures

Vol % of MeOH	25℃	30℃	35℃	40℃
0.000	0.0167	0.0205	0.0236	0.0302
0.047	0.0206	0.0239	0.0292	0.0367
0.10	0.0239	0.0268	0.0318	0.0395
0.151	0.0275	0.0315	0.0342	0.0419
0.228	0.0303	0.0345	0.0366	0.0429
0.323	0.0325	0.0389	0.0408	0.0483
0.400	0.0352	0.0439	0.0467	0.0558
0.509	0.0397	0.0470	0.0489	0.0580
0.640	0.0459	0.0509	0.0529	0.0609
0.800	0.0518	0.0550	0.0584	0.0651
1.000	0.0562	0.0594	0.0652	0.0759

From the relation of (-log C) versus 1/T, the enthalpy of solvation (ΔH_s) are calculated where the slope equals ΔH_s /2.303 R. From the values of ΔG_s.

$$\Delta G_t = \Delta G_s - \Delta G_w \qquad (3)$$

Where ΔG_s and ΔG_w are the solvation free energies in mixed solvent and water as reference solvent and ΔH_s the values of $T\Delta S_s$ of solvation at 25℃ can be calculated using Gibbs equation (4):

$$\Delta G_s = \Delta H_s - T\Delta S_s \qquad (4)$$

The calculated values of the different thermodynamic salvation parameters (ΔG_s, ΔH_s and $T\Delta S_s$) for DB18C6 in mixed MeOH–H_2O solvents at 25℃ were tabulated in Table (2) together with their transfer values ΔG_t , ΔH_t & $T\Delta S_t$ from mixed solvent to water as standard solvent[16].

Table 2. The solvation free energies (ΔG_s), enthalpy of solvation (ΔH_s), entropy of solvation ($T\Delta S_s$) and their transfer values ΔG_t & ΔH_t & $T\Delta S_t$ for DB18C6 in mixed MeOH-H_2O solvents 25℃ (in KJ / mole)

Vol % of MeOH	ΔG_s	ΔG_t	ΔH_s	ΔH_t	$T\Delta S_s$	$T\Delta S_t$
0	10.129	0	31.112	0	41.241	0
10	9.609	0.520	29.870	-1.242	34.479	-1.762
20	9.242	0.887	24.891	-6.221	34.133	-7.108
30	8.894	1.235	23.894	-7.218	32.788	-8.453
40	8.654	1.475	22.540	-8.572	31.194	-10.047
50	8.481	1.648	21.500	9.612	29.981	-11.260
60	8.283	1.846	21.810	-9.302	30.093	-11.148
70	7.985	2.144	21.182	-9.930	29.169	-12.072
80	7.626	2.503	21.026	-10.086	28.652	-12.589
90	7.327	2.802	19.026	-12.086	26.353	-14.888
100	7.125	3.004	14.852	-16.260	21.477	-19.264

It was observed from Table (2) that by more increasing the percentage of MeOH in the mixed solvents the transfer free energies, enthalpies and entropies of solvation of DB18C6 increase in their negative values favouring more solvation behaviour.

The measured refractive indices for the saturated DB18C6 solutions in MeOH–H_2O solvents are shown in Table (3). The plot of refractive index versus absolute temperature follows a linear law

$$n_d = C + DT \qquad (5)$$

Table 3. Refractive indices (n_d) for DB18C6 in mixed MeOH−H_2O solvents at different temperatures and C, D factors for equation (5)

Vol% of MeOH	n_d				C	$D \times 10^4$
	25℃	30℃	35℃	40℃		
0	1.3332	1.3326	1.3319	1.3312	1.3337	-5
20	1.3368	1.3364	1.3355	1.3348	1.3374	-5.4
40	1.3408	1.3398	1.3388	1.3376	1.3417	-6.4
60	1.3420	1.3404	1.3388	1.3368	1.3434	-6.8
80	1.3390	1.3372	1.3365	1.3227	1.3402	-7.8
100	1.3304	1.3276	1.3255	1.3222	1.3313	-8.8

By means of least–squares method it was found C and D values are given in Table 3 also with error of C and D ± 0.003 and error for n_d is ±0.02%. The observed D values increase in their values whereas C values are almost constant indicating more solvent effect by increasing percentage of MeOH.

From Clausius – Mosotti and Maxwell derivation[17] a relationship connecting the dielectric constant of a substance with its refractive index for low frequency radiation namely n^2_d as in case of DB18C6, so that, the molar refraction (R) equal the molar polarization (P) which may be equated by:

$$P = R = \frac{n^2 - 1}{n^2 + 2} Vm \qquad (6)$$

$$Vm = \frac{\varepsilon^2 - 1}{\varepsilon^2 + 2} = \frac{4\pi N\alpha}{3} \qquad (7)$$

Where R, molar refraction, P molar polarization, n (n_d) refractive index, ε, dielectric constant, V_m molar volume (M/d), α the polarizability and N is Avogadro's number. The molar volumes V_m, P and α for saturated solutions of DB18C6 in mixed MeOH–H_2O solvents are presented in Table (4) at different temperatures. This results indicates the increase in their values with more increasing MeOH content in the mixtures favouring more solvaton behavior.

The molar refraction for DB18C6 was calculated in its solid state from the summation of bond refraction[18] and was found to be 57.626. Also the standard polarizability for solid DB18C6 was calculated by adding the bond polarizabilities and found to be 2.12x 10^{-23} C.C/mole. In comparing these values with values in Table (4), it was found that increase in molar polarization and polarizabilies for DB18C6 on mixed MeOH–H_2O solvents.

On drawing the relation between P versus 1/T straight lines were obtained (Fig.1) with slope B and intercept equal to the sum of atomic polarization (P_A) and electronic polarization (P_E)[17]. The dipole moment can be calculated by using equation 8:

$$\mu = 0.0181 \sqrt{B} \qquad (8)$$

Table 4. Molar volumes (v_m), molar polarization P and Polarizabilities (α) for DB18C6 in mixed MeOH–H_2O mixtures at different temperatures

Vol%of MeOH	V_m (cm³/mole)				P (c.c / mole)			
	25℃	30℃	35℃	40℃	25℃	30℃	35℃	40℃
0	354.73	355.43	356.49	364.14	73.006	73.150	73.108	74.554
20	364.050	367.69	368.93	370.62	74.737	74.411	75.461	76.112
40	376.84	380.52	382.60	385.10	79.158	79.723	79.941	80.204
60	389.13	396.62	403.77	408.23	82.000	83.224	84.364	85.047
80	404.05	411.28	418.11	428.51	85.566	85.566	86.823	85.651
100	451.24	454.37	457.08	460.21	92.159	92.084	92.092	91.866

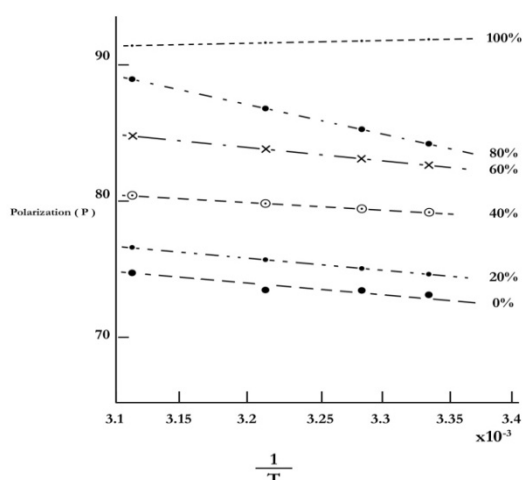| Vol%of MeOH	α (X10^{23}c.c / mole)			
	25℃	30℃	35℃	40℃
0	2.894	2.899	2.898	2.954
20	2.962	2.949	2.991	3.017
40	3.138	3.160	3.169	3.179
60	3.250	3.299	3.344	3.371
80	3.348	3.392	3.882	3.375
100	3.653	3.650	3.650	3.641

Figure 1. Polarization of saturaled solutions of DB18C6 in mixed MeOH-H_2O solvents

and their values are listed in Table (5). Also, from the intercepts the values of $P_A + P_E$ are calculated and tabulated in Table (5). Also, small effect of solvent on the dipole moment of DB18C6 was observed while very influenced effect on $P_A + P_E$ can be understood.

The difference between the molar polarization and the sum of $P_A + P_E$ gives the orientation polarization P_o, which will be small for DB18C6 due to its lower dipole moment values in mixed MeOH–H_2O solvents.

Table 5. Induced Dipole moment μ_i, $P_A + P_E$ (atomic and electronic polarizations), Polarization permittivity (ε_∞) and solubility parameters (δ) for DB18C6 in mixed MeOH–H_2O Solvents at 25℃ .

Vol%of MeOH	μ_i (x 10^{-18} esu)	$P_A + P_E$ (c.c/mole)	ε_∞	J.cm^{-3} δ
0	1.451	74.6	1.866	7.029
20	1.551	76.4	1.876	6.939
40	1.645	80.4	1.888	6.820
60	1.939	85.5	1.891	6.755
80	2.228	89.4	1.883	6.587
100	0.949	91.7	1.858	6.233

The decrease in entropy and entropy of transfer values for DB18C6 by more increasing the percentage of MeOH shown

in Table (2) is also an evidence that the orientation polarization and the dipole moments decrease in the same order because they are dependent on each other.

The refractive index gives the contribution of the electronic polarization to permittivity $\varepsilon \infty$. The contribution of the atomic polarization can by estimated for organic molecules approximately by[18,19]:

$$\varepsilon_\infty = 1.05 \ n^2_d \tag{9}$$

The calculated ε_∞ values for DB18C6 are presented also in Table (5) at 25℃ in mixed MeOH–H$_2$O solvents indicating its small effect. The differential scanning calorimeter (DSC) was used to evaluate the heat of vaporization (ΔH_v) of DB18C6 in solid state and was found to be 75.7 J/mole with one endothermic peak at 273.2℃ (Fig. 2), having the order of 0.46. This verify the heat of solvation values given in Table (2) with also an endothermic behavior of solvation.
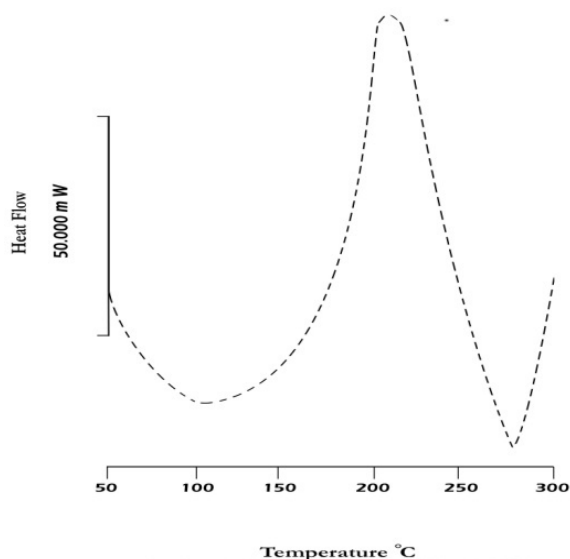

Figure 2.   DSC diagram for solid DB18C6

From the heat of evaporization (ΔH_v), the solubility parameters (equation 10) for the ether used were calculated by the use of Hildebrand equation[19]:

$$\delta = \left(\frac{\Delta H_v - RT}{v_m} \right)^{\frac{1}{2}} \tag{10}$$

The calculated δ values are given also in Table (5) with its small effect on illustrating the solvent mole in solvation processes. Therefore, increasing the mole fraction % of methanol (organic solvent)[20-22] increases the solubility of DB18C6 in mixed MeOH–H$_2$O solvents due to the increase of molecule- solvent interactions. These molecules – solvent interactions were explained by increase in molar volumes, total polarization, polarizabilites, electronic and atomic polarizations.

4. Conclusions

All the solubility and thermodynamic parameters for dibenzo-18-crown-6 are increased by increasing methanol percentage in the mixed methanol-water solvents. This work give a lot of data about this wide range polycompound for helping in its uses and applications.

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