Dielectric absorption in dilute solutions of dibenzo-18-crown-6 in 1,4-dioxane

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Dielectric absorption of dibenzo-18-crown-6 (DB18C6) in solutions of 1,4-dioxane have been studied at 9.1 GHz frequency at three different temperatures 293.15, 303.15 and 313.15 K. A single frequency concentration variation method of Gopalkrishna was used to calculate relaxation time (τ_{GK}). Thermodynamical parameters, like free energy (ΔF), enthalpy (ΔH) and entropy (ΔS) of activation for the dielectric relaxation have been determined using dielectric data. Static permittivity, refractive index and density of liquid solutions are also measured at 293.15 K. Dipole moment of DB18C6 is determined using Gopalkrishna and Guggenheim's method.

Keywords: Dibenzo-18-crown-6, 1,4-Dioxane, Relaxation time, Dipole moment, Static permittivity, Refractive index

1 Introduction

Investigations of dielectric properties of materials or molecules provide information about the structure of the molecules. This information is required in many areas of science and technology. In recent past, many workers have tried to obtain information regarding inter and intra-molecular interactions in the binary and ternary mixtures of molecular systems of industrial, biological and pharmaceutical importance¹⁻⁷.

Motivation behind this work is to expand the knowledge on dielectric characterization in organic liquid systems and apply it to a very important group of supra-molecular system called crown ethers. Supra-molecules are considered to be the chemical building blocks of the future because of their widespread applications from quantum dots to biomedicine and bioinformatics and from artificial intelligence to virtual reality⁸.

Literature survey implies that no much work on dielectric properties of the crown ethers is done at lower frequency or at microwave frequencies. An investigation was carried out by Andjelic⁹ on the dipole dynamics of low molecular weight ether series namely 12-crown-4, 15-crown-5 and 18-crown-6 by dielectric relaxation spectroscopy (DRS). Patil *et al.*¹⁰ carried out dielectric studies of 18-crown-6 (18C6) in CCl₄ solutions. They measured static permittivity, permittivity at optical frequency and density of the dilute solutions of 18C6 at 298.15 K and obtained the

dipole moment of 18C6. The derived dipole moment value was discussed on the basis of conformation and the properties of 18C6. The dielectric properties of dibenzo-18-crown-6 (DB18C6), a member of crown ether family, have not been studied so far. This fact has prompted to study the dielectric properties of DB18C6.

Primary uses of crown ethers are separation of inorganic salts by use of various crown ethers, liquid-liquid extraction, liquid-membrane separation, ion sensitive electrodes and organic synthesis as phase transfer reagents¹¹⁻¹⁴. Their characteristic properties are their ability to solubilize inorganic compounds in organic solvents and thus, increase the range of their reactivity.

The most common crown ethers are oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e. $(-CH_2CH_2O_{-})_n$. DB18C6 was the first born amongst the family of macro cyclic polyethers described by Pedersen. This simple molecule has ability to form complexes with alkali and alkaline earth metal cations and with ammonium ions.¹⁵⁻¹⁷

1,4-Dioxane is a clear, colourless heterocyclic organic compound, which is a liquid at room temperature and pressure. It is commonly used as a protic solvent. It is classified as ether, with each of its two oxygen atoms forming an ether functional group. It is more polar than diethyl ether. It is primarily used as solvent. It also finds its application as fumigants and automotive coolant, and as an internal standard for calibrating chemical shifts in NMR¹¹.

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In the present investigation, some dielectric properties of DB18C6 in 1,4-dioxane solutions were studied. The measurements were carried out in two parts. First, the measurements of complex permittivity of DB18C6 in 1,4-dioxane solutions were carried out microwave frequency, at three at different temperatures (293.15, 303.15 and 313.15 K) and from the data. the relaxation time and thermodynamical parameters were calculated. Secondly, the measurements of static permittivity, refractive index and density of DB18C6 in 1,4-dioxane solutions were carried out at 293.15 K to determine its dipole moment.

2 Experimental details and Data analysis

2.1 Sample preparation

DB18C6 (assay purity 98%), from Sigma-Aldrich, was procured by Department of Chemistry, Gujarat University, Ahmedabad (India). The contact with atmospheric moisture was avoided by handling DB18C6 in air tight bottle. All the solutions were made in 1,4-dioxane by weight in glass stopper bottles. Dilute solutions were made up of different weight fractions (0.0017, 0.0029, 0.005, and 0.0073) of DB18C6. Digital balance with accuracy ± 0.0001 g was used to prepare the samples.

2.2 Complex permittivity at microwave frequency

Complex permittivity of sample solutions were measured in the dilute solutions of 1,4-dioxane using X-band microwave test bench operated at fixed frequency of 9.1 GHz. The cell containing experimental liquid was kept vertical and connected to the main transmission line by E-plane band. In the microwave bench, the liquid filled portion of the cell was separated from the rest of the microwave line by a thin sheet of mica. A short-circuiting reflecting plunger was used to vary the length of the liquid column. The energy waves from klystron source enter to the waveguide then passed through the liquid and was reflected back by a short circulating plunger. Thus, a standing wave pattern was set up. A method suggested by Gowri Krishna et al.¹⁸ was used for the measurement of complex permittivity. In this method, plunger was kept at Z = 0 (mica sheet) and slotted line probe was moved till the micrometer connected to the crystal detector registered a maximum current. Now keeping the slotted line probe at this position, the shorting plunger was moved back and the standing wave power was recorded for different sample thickness. Such measurements were carried out at three different temperatures (293.15, 303.15 and 313.15 K) for each sample. Then experimental data points were fitted to the equation to obtain values of the fitting parameters α , β and δ (Ref 18):

$$IEI^{2} = E_{0}^{2} [1 + \exp(-4\alpha d) + 2 \exp(-2\alpha d) \cos(2\beta d - \delta)]$$
...(1)

where, E_0 is the amplitude of the incident wave; E is the amplitude of the resultant wave in the air medium; α is the attenuation constant; β is the phase constant; δ is the phase shift involved in reflection; and d is the liquid column length. CurveExpert software was used to fit the experimental data points.

The best fit curves obtained after fitting the experimental data points to Eq. (1) for 1,4-dioxane and 0.0017 weight fraction of DB18C6 in 1,4-dioxane solutions are shown in Figs 1 and 2, respectively. Similar plots are obtained for each sample. The best fit values of α and β are used to calculate ε' and ε'' from the following equations:



Fig. 1 — Experimental data points fitted to Eq. (1) for 1,4-dioxane at 293.15 K (solid line shows fitted curve)



Fig. 2 — Experimental data points fitted to Eq. (1) 0.0017 weight fraction of DB18C6 in 1,4-dioxane solutions at 293.15 K (solid line shows fitted curve)

$$\boldsymbol{\varepsilon}' = \boldsymbol{\lambda}_0^2 \left[\frac{1}{\boldsymbol{\lambda}_c^2} + \frac{\boldsymbol{\beta}^2 - \boldsymbol{\alpha}^2}{4\pi^2} \right] \qquad \dots (2)$$

$$\varepsilon'' = \frac{\lambda_0^2 \alpha \beta}{2\pi^2} \qquad \dots (3)$$

where, λ_0 and λ_c , are the free space and cut off wavelengths, respectively.

Values of fitting parameters α , β and complex permittivity of the solutions of DB18C6 in the 1,4-dioxane are presented in Table 1.

Dielectric relaxation time (τ_{GK}) was then calculated using a single frequency concentration variation Gopalkrishna's method¹⁹. In this method, first the quantities X and Y were calculated using the equations:

$$X = \frac{\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad \dots (4)$$

$$Y = \frac{3\varepsilon''}{(\varepsilon'+2)^2 + {\varepsilon''}^2} \qquad \dots (5)$$

After calculating *X* and *Y*, a graph of *X* against *Y* is plotted, which is a straight line satisfying the following equation:

$$X = P + \frac{1}{\omega \tau_{GK}} Y \qquad \dots (6)$$

Then relaxation time, τ_{GK} , is computed from the slope of the straight line. A typical plot of *X* versus *Y* at 293.15 K is shown in Fig. 3. Thermodynamical parameters such as free energy of activation (ΔF), enthalpy (ΔH) and entropy of activation (ΔS) are calculated using Eyring's rate equations²⁰.

2.3 Measurement of static permittivity

The values of static permittivity of liquid samples were determined using capacitive measurement method with a short compensation at 2 MHz. A precision LCR meter (Agilent 4980) with a four terminal liquid dielectric test fixture (Agilent 16452A) was used for the capacitance measurement of the cell without and with sample at a fixed frequency of 2 MHz.

2.4 Measurement of refractive index

Refractive indices of samples were measured by Abbe's refractometer having an accuracy of ± 0.0001 . The permittivity at optical frequency was calculated from the square of refractive index.



Fig. 3 — Variation in quantity X with Y at 293.15 K

Table 1 — Values of fitting parameters α , β , δ , and complex permittivity (ϵ' , ϵ ") of solutions of DB18C6 in 1,4-dioxane at different temperatures

Wt Fr of DB18C6	Attenuation constant (α)	Phase constant (β)	Dielectric constant (ɛ')	Dielectric loss (ɛ")
Temp= 293.15 K				
0.000	0.040	2.659	2.467	0.058
0.002	0.041	2.659	2.468	0.059
0.003	0.042	2.659	2.468	0.060
0.005	0.044	2.661	2.471	0.064
0.007	0.045	2.668	2.481	0.066
Temp= 303.15 K				
0.000	0.030	2.620	2.411	0.043
0.002	0.032	2.632	2.429	0.046
0.003	0.035	2.641	2.442	0.051
0.005	0.037	2.646	2.448	0.053
0.007	0.040	2.248	2.451	0.058
Temp.= 313.15 K				
0.000	0.030	2.605	2.405	0.042
0.002	0.030	2.624	2.417	0.043
0.003	0.034	2.639	2.439	0.049
0.005	0.035	2.641	2.442	0.050
0.007	0.036	2.243	2.444	0.051

2.5 Measurement of density

Density of liquid samples was measured using double arm pycnometer and a capillary bore with an internal diameter of 1 mm. The densities are accurate to ± 0.1 kg m⁻³. The temperature of the sample was maintained at the required constant value by using temperature bath controlled by thermostat with an accuracy of ± 0.1 K.

Determined values of static permittivity (ϵ_0), permittivity at optical frequency (ϵ_{∞}) and density (ρ) of the liquid samples at 293.15 K are presented in Table 2. Dipole moment of DB18C6 at 293.15 K is calculated using the Gopalkrishna¹⁹ (μ_{GK}) and Guggenheim's²¹ (μ_G) methods.

3 Results and Discussion

Determined values of relaxation time. thermodynamical parameters and dipole moment of DB18C6 in 1,4-dioxane solutions are presented in Table 3. From the table, it can be seen that the value of relaxation time of DB18C6 in 1,4-dioxane at 293.15 K is 20.99 ps. Such a higher value suggests that the molecule of DB18C6 is large in size. Furthermore. the solvent 1.4-dioxane. which itself is slightly polar having a small dipole moment value of 0.45 D (Ref. 10) produces the

Table 2 — Values of static permittivity, permittivity at optical
frequency and density of the solutions of DB18C6 in 1,4-dioxane
at 293.15 K

Wt Fr of DB18C6	Static Permittivity (ϵ_0)	Permittivity at optical frequency (ϵ_{∞})	Density, g cm ⁻³
0.000	2.372	2.039	1.030
0.002	2.385	2.044	1.036
0.003	2.390	2.053	1.039
0.005	2.413	2.056	1.041
0.007	2.425	2.057	1.044

Table 3 — Values of relaxation time, thermodynamical parameters and dipole moment of DB18C6 in 1,4-dioxane

Temp (K)) Relaxation	Ther	nodyna	mical	Dipole
	time $T_{\rm GK}$ (ps)	parameters			moment μ (D)
		ΔF (kcal mol ⁻¹)	ΔH (kcal mol ⁻¹)	ΔS (Cal mol ⁻¹ K ⁻¹))
293.15	20.99	2.82	15.22	0.0423	$\mu_G =$
					2.1(293.15 K)
303.15	11.77	2.59		0.0417	$\mu_{GK} =$
					2.5(293.15 K)
313.15	4.3	2.07		0.0420	

polar environment introducing local strains that impede the relaxation process giving rise to the large value of relaxation time of DB18C6. The relaxation time decreases with increase in the temperature. This is due to the fact that with increasing temperature, there is an increase in the thermal agitation of the system, which results in lowering down the frictional resistance for dipolar rotation and thus, decreasing the values of relaxation time²².

A plot of ln ($T\tau_{GK}$) versus 1/T of DB18C6 exhibits linear relationship (Fig. 4) suggesting that the decay of relaxation time with temperature is exponential. These relationships, therefore, can be represented by the rate process. Accordingly, the molar free energy (ΔF) , the molar free enthalpy (ΔH) and the molar entropy (ΔS) of the activation can be evaluated from Eyring's equation²⁰. For most liquids and solutions, values of change in enthalpy are in the range 2-4 kcal mol⁻¹ (Ref. 23); but in the present study, ΔH value for DB18C6 is high, 15.22 kcal mol⁻¹. This is quite expected as the molecule is of large size and thus, experiences higher intrinsic viscosity in dipole rotation. Enthalpy of activation has much higher value than the free energy and hence, resulting in small positive value of the entropy of activation. Entropy of the system is the measure of the orderly nature of the system as explained by Branin and Smyth²⁴. If the environment of the system is co-operative for activated process, the positive value of change in entropy for activated process indicates the non-co-operative environment of the system and activated state is unstable. In the present case, it is observed that the change in entropy for dielectric process is positive indicating the unstable state.



Fig. 4 — Variation in $\ln(T.\tau_{GK})$ with 1/T

In the present investigation, dipole moment of DB18C6 in 1.4-dioxane at 293.15 K, obtained using Gopalkrishna (μ_{GK}) and Guggenheim (μ_{G}) methods are found to be 2.5 D and 2.1 D, respectively. Though these values are in moderate agreement, the slight variation may be due to different methods used to determine dipole moment. Many researchers have determined dipole moment of 18C6 molecule, in different solvents and at different temperatures, experimentally or through molecular simulation study^{10,25-28}. Literature survey suggests that dielectric properties of DB18C6 remain poorly studied, and the reported value of its dipole moment could not be found to compare with the present value. The 18C6 is non-benz-annulated macroxyclic poly ether (crown ether) molecule, whereas DB18C6 has two benzene rings on the opposite sides of the crown ether $ring^{29}$. Therefore, symmetry in the structure of DB18C6 is still maintained. Therefore, a comparative study of 18C6 and DB 18C6 can throw some light on the structural features of DB18C6. Through the molecular dynamics study of structure of 18C6 in vacuo and in cyclohexane, Leuwerink and Briels²⁵ found that the crown ether, on an average, displays an elliptical shape, and that the solvent slows down the dynamics of the crown ether molecule. Perrin et al.²⁶ measured dipole moment of liquid 18C6 over a range of temperatures and concluded that the molecule adopts various conformations and that the populations of these conformations are temperature dependent. Through the Monte Carlo study, Ha and Chakraborty²⁷ found that the temperature and solvent polarity have a large effect on the 18C6 structure. Experimental work of Caswell and Suvannunt²⁸ also suggest the existence of mixtures of conformations of 18C6. Patil *et al.*¹⁰ carried out dipole moment study of 18C6 (18-crown-6) in CCL₄ solutions at 298.15 K and obtained 3.51D value of dipole moment of 18C6. From the symmetry considerations, Patil et al.¹⁰ pointed out that for 18C6 in C_i, conformation should have zero value of dipole moment. However, it was argued that the high value of the dipole moment probably can be attributed to the presence of flexibility of the crown ring, which leads to the existence of conformational dynamic equilibrium. Other interpretation of high value of dipole moment is due to the existence of 18C6 in C_x (i.e. having a mean plane of reflection) symmetry point group (or of C₃ type), which leads to a finite value of μ . Considering symmetrical structure of DB18C6, zero value of

dipole moment is expected. But experimentally determined large value of dipole moment of DB18C6 confirms that it also is a highly flexible molecule that can adopt many different conformations depending on the environment.

Conclusions

absorption of dibenzo-18-crown-6 Dielectric (DB18C6) in solutions of 1.4-dioxane have been studied at 9.1 GHz frequency at three different temperatures. Thermodynamical parameters, like free energy (ΔF), enthalpy (ΔH) and entropy (ΔS) of activation for the dielectric relaxation have been determined. The relaxation time decreases with increase in the temperature. The decay of relaxation time with temperature is exponential. In the present case, it is observed that the change in entropy for dielectric process is positive indicating the unstable state. The high value of the dipole moment probably can be attributed to the presence of flexibility of the crown ring. The experimentally determined large value of dipole moment of DB18C6 confirms that it is also a highly flexible molecule that can adopt many different conformations depending on the environment.

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