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Thermodynamic and Viscometric Study of Calix (6) Arene and their Derivatives

Rakhi R. Kale and Yogita S. Thakare*
Department of Chemistry, Shri Shivaji Science College, Amravati, MS, India
yogitathakare_2007@rediffmail.com

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Abstract

Viscosity measurement of calix(6)arene, their acetyl and benzoyl derivatives were carried out in xylene and cyclohexane. The study was implemented for several variation in concentration as well as temperature of solute in solvent. From the experimental data, molecular interactions of different derivative of calix(6)arene in terms of viscosity B – coefficient were studied at 303 K. Also, the thermodynamic parameters ΔG, ΔH, ΔS have been evaluated by studying the relative viscosity at different temperature and concentration.

Keywords: Viscosity, Thermodynamic parameters, Molecular interaction, Calixarene derivatives..

Introduction

Calixarenes are macrocyclic compounds composed of phenolic units connected by methylene bridges to form a hydrophobic cavity that is capable of forming inclusion complexes with a variety of molecules. Calixarenes are cyclic oligomers formed by the base-catalysed condensation of formaldehyde and p-tert-butylphenol[1-2]. The cavity sized can be varied by substituting lower rim[3-7].

For natural and industrial processes known significant physicochemical properties are density, viscosity, and surface tension of liquids. Viscosity implies resistance to flow. Viscosity measurement provides useful information about solute-solute and solute-solvent interactions in non aqueous and aqueous solvents. The Jones-Dole equation accounts for the observed viscosity concentration dependence of dilute electrolyte solutions, while Breslau-Miller, Vand, Moulik, Thomson and Einstein equations account for the concentration dependence of viscosity in concentration of electrolyte solutions[8-13].

The present work deals with the viscosity study of calix(6)arene, their acetyl and benzoyl derivative in xylene and cyclohexane at different concentrations and at different temperature 303, 313, 323 K. From the experimental data relative viscosity and viscosity-coefficient is compute which was further used to calculated thermodynamic parameters.

Methodology

The p-t-butyl calix(6)arene was synthesized by base catalyzed reaction between tertiary butyl phenol and formaldehyde[1]. Acetyl derivative and benzoyl derivative of it prepared and was characterized by ^{1}HNMR, ^{13}C NMR, Mass and IR spectroscopy[14-15].

Standard solutions of p-t-butyl calix(6)arene, hexaacetato calix(6)arene and hexabenzoyl derivatives were prepared in various diluents such as xylene and cyclohexane, etc by diluting it to the known volume with the required diluents. For viscosity measurements cleaned, dried Ostwald's viscometer were used throughout the experimental work.

Results and Discussion

The values of density and relative viscosity of calix(6)arene and their derivatives increases with increase in concentration of the solutes. The increase in viscosity with increase in concentration may be attributed to the increase in solute-solvent interactions. Solutes are surrounded by solvent molecules and the degree of cluster formation is less. They behave as structure breakers. Viscosity data were analyzed in the light of Jones-Dole equation.

$$(\eta r - 1) / \sqrt{C} = A + B\sqrt{C}$$

Where: A and B are the Falkenhagen and the Jones-Dole coefficients.

From the graph of $(\eta_r - 1) / \sqrt{C}$ verses $\sqrt{C}$, 'A' which is the measure of solute – solute interactions and 'B' which is the measure of solute – solvent interactions has been calculated.

From Jones-Dole equation negative values of 'A' coefficient shows very weak solute-solute interactions. Above table also replicates this result again this interactions further decreases with an increase temperature as well as molarity of calix(6)arene derivative in the solution. The slope of straight line gave value of β -coefficient. Table shows that the values of the ' B' coefficient for calix(6)arene and their derivatives in the studied solvent systems are positive, thereby suggesting the presence of strong solute-solvent interactions.

The viscosity of a liquid generally decreases with rise in temperature. The graphs are plotted between log η_r and 1/T. The graph for each system gives linear straight line showing the validity of equation. The thermodynamic parameters were calculated by using expression $\Delta G = -2.303\ R \times$ slope, $\log \eta_{r1} - \log \eta_{r2} = [\Delta H / 2.303]\ [1/T1 - 1/T2]$ and $\Delta S = (\Delta G - \Delta H) / T$.

Table-1
Thermodynamic study with variation in concentration

System	Temp (K)	Conc. (M)	*Medium- Cyclohexane*					*Medium-Xylene*		
			Relative Viscosity η_r	Specific Viscosity $\eta r - 1/\sqrt{C}$	A coefficient	B coefficient	Relative Viscosity η_r	Specific Viscosity $\eta r - 1/\sqrt{C}$	A coefficient	B coefficient
p-tert butyl calix(6)arene	303K	0.001	0.604	-12.77	-48.69	12.34	0.785	-6.9	-62.36	19.2
		0.0005	0.616	-17.45			0.713	-13.04		
		0.0001	0.619	-38.1			0.538	-46.2		
Benzoyl derivative of calix(6)arene	303K	0.001	0.626	-12.06	-43.77	10.51	0.515	-15.65	-65.07	19.11
		0.0005	0.641	-16.32			0.491	-23.14		
		0.0001	0.658	-34.2			0.45	-54.91		
Acetyl derivative of calix(6)arene	303K	0.001	0.593	-13.13	-44.24	10.82	0.517	-15.58	-72.84	16.94
		0.0005	0.622	-17.18			0.505	-22.5		
		0.0001	0.653	-34.7			0.496	-50.4		

Table-2
Thermodynamic study with variation in temperature (medium - xylene)

System	Conc. (M)	Temp (K)	1 / T (K^{-1}) × 10^{-3}	Time flow (sec.)	Density (ρ) g.cm-3	Relative Viscosity η_r	Log (η_r)
p-t-butyl of calix (6)arene	0.001	303	3.30 ×10^{-3}	53	0.84	0.628	-0.202
		313	3.19 × 10^{-3}	22	0.749	0.232	-0.634
		323	3.09 × 10^{-3}	21	0.739	0.215	-0.667
	0.0005	303	3.30 ×10^{-3}	48	0.842	0.57	-0.244
		313	3.19 × 10^{-3}	21	0.735	0.217	-0.664
		323	3.09 × 10^{-3}	20	0.732	0.203	-0.692
	0.0001	303	3.30 ×10^{-3}	36	0.847	0.43	-0.367
		313	3.19 × 10^{-3}	19	0.722	0.193	-0.714
		323	3.09 × 10^{-3}	18	0.713	0.118	-0.75
Acetyl derivative of calix (6)arene	0.001	303	3.30 ×10^{-3}	47	0.745	0.494	-0.306
		313	3.19 × 10^{-3}	29	0.65	0.265	-0.577
		323	3.09 × 10^{-3}	18	0.64	0.16	-0.795
	0.0005	303	3.30 ×10^{-3}	34	0.841	0.403	-0.395
		313	3.19 × 10^{-3}	22	0.754	0.233	-0.633
		323	3.09 × 10^{-3}	21	0.747	0.218	-0.662
	0.0001	303	3.30 ×10^{-3}	33	0.849	0.395	-0.403
		313	3.19 × 10^{-3}	20	0.748	0.21	-0.678
		323	3.09 × 10^{-3}	19	0.74	0.195	-0.71
Benzoyl derivative of calix(6)arene	0.001	303	3.30 ×10^{-3}	35	0.853	0.421	-0.376
		313	3.19 × 10^{-3}	23	0.76	0.246	-0.609
		323	3.09 × 10^{-3}	20	0.756	0.21	-0.678
	0.0005	303	3.30 ×10^{-3}	35	0.845	0.393	-0.406
		313	3.19 × 10^{-3}	20	0.756	0.213	-0.672
		323	3.09 × 10^{-3}	19	0.751	0.198	-0.703
	0.0001	303	3.30 ×10^{-3}	30	0.835	0.353	-0.452
		313	3.19 × 10^{-3}	21	0.73	0.216	-0.666
		323	3.09 × 10^{-3}	18	0.743	0.186	-0.73

Table-3
Thermodynamic study with variation in temperature (medium - cyclohexane)

System	Conc. (M)	Temp (K)	1 / T (K^{-1}) × 10^{-3}	Time flow (sec.)	Density (ρ) g.cm-3	Relative Viscosity η_r	Log (η_r)
p-t-butyl of calix (6)arene	0.001	303	3.30 ×10^{-3}	45	0.76	0.483	-0.316
		313	3.19 × 10^{-3}	25	0.671	0.236	-0.627
		323	3.09 × 10^{-3}	23	0.655	0.209	-0.679
	0.0005	303	3.30 ×10^{-3}	46	0.758	0.492	-0.308
		313	3.19 × 10^{-3}	27	0.656	0.249	-0.604
		323	3.09 × 10^{-3}	24	0.653	0.217	-0.664
	0.0001	303	3.30 ×10^{-3}	47	0.745	0.494	-0.306
		313	3.19 × 10^{-3}	29	0.65	0.265	-0.577
		323	3.09 × 10^{-3}	18	0.64	0.16	-0.795
Acetyl derivative of calix (6)arene	0.001	303	3.30 ×10^{-3}	44	0.763	0.474	-0.324
		313	3.19 × 10^{-3}	26	0.651	0.238	-0.623
		323	3.09 × 10^{-3}	22	0.649	0.198	-0.703
	0.0005	303	3.30 ×10^{-3}	46	0.765	0.497	-0.304
		313	3.19 × 10^{-3}	27	0.649	0.246	-0.609
		323	3.09 × 10^{-3}	23	0.644	0.205	-0.688
	0.0001	303	3.30 ×10^{-3}	48	0.77	0.521	-0.283
		313	3.19 × 10^{-3}	29	0.621	0.253	-0.597
		323	3.09 × 10^{-3}	24	0.637	0.212	-0.674
Benzoyl derivative of calix (6)arene	0.001	303	3.30 ×10^{-3}	46	0.77	0.5	-0.301
		313	3.19 × 10^{-3}	25	0.736	0.259	-0.587
		323	3.09 × 10^{-3}	23	0.719	0.229	-0.64
	0.0005	303	3.30 ×10^{-3}	47	0.772	0.512	-0.291
		313	3.19 × 10^{-3}	33	0.73	0.339	-0.47
		323	3.09 × 10^{-3}	29	0.717	0.288	-0.541
	0.0001	303	3.30 ×10^{-3}	48	0.776	0.526	-0.28
		313	3.19 × 10^{-3}	30	0.714	0.301	-0.521
		323	3.09 × 10^{-3}	27	0.709	0.266	-0.575

Table-4
Values of thermodynamic parameters in xylene medium

System	Concentration (M)	ΔG (J $mole^{-1}$)	ΔH (J $mole^{-1}$)	ΔS (J $mole^{-1}K^{-1}$)
p-t-butyl calix(6)arene	0.001M	45517.10	9044.51	120.37
	0.0005M	42889.6	8793.27	112.53
	0.0001M	36666.78	7264.92	97.04
Acetyl derivative of calix(6)arene	0001M	24316.87	4710.68	64.71
	0.0005M	25561.43	4982.85	67.92
	0.0001M	30348.22	5757.5	81.16
Benzoyl derivative of calix(6)arene	0001M	28912.18	4878.17	79.32
	0.0005M	28433.5	4569.07	75.46
	0.0001M	26614.53	4480.38	73.05

Table-5
Values of thermodynamic parameters in cyclohexane medium

System	Concentration (M)	ΔG (J mole^{-1})	ΔH (J mole^{-1})	ΔS (J mole^{-1}K^{-1})
p-t-butyl calix(6)arene	0.001M 0.0005M 0.0001M	34752.06 34781.91 46814.76	6511.21 6197.16 5673.75	93.20 94.03 135.78
Acetyl derivative of calix(6)arene	0001M 0.0005M 0.0001M	36283.83 36762.51 37432.66	6259.97 6385.59 6574.02	99.09 100.25 101.84
Benzoyl derivative of calix(6)arene	0001M 0.0005M 0.0001M	32454.41 28933.93 23242.03	5862.18 5747.61 5045.66	87.76 76.62 67.55

Conclusion

In present study, results shows that positive values of viscosity 'B' coefficient for calix(6)arene and it's derivative indicates the presence of strong solute-solvent interactions. In macrocyclic compound or in polymer relative viscosity may be negative because the polymer is breaking up some sort of weak network in the solvent (hydrogen bonding, polar-polar interaction) so that the solvent has a lower viscosity, thus leading to the negative intrinsic viscosity[16]. Thermodynamic parameters change in enthalpy (ΔH), change in entropy (ΔS) and change in free energy (ΔG) were determined from the viscosity values at different temperature. For all tested ligands the positive value of ΔH indicates the reaction is endothermic. For calix(6)arene, using xylene as a solvent the change in free energy (ΔG)and the change in entropy (ΔS) decreases with decrease in concentration, while using cyclohexane as a solvent shows opposite results. For acetyl derivative in both the solvent shows the values of (ΔG) and (ΔS) increases with decrease in concentration. On the other hand, in benzoyl derivative the values of (ΔG) and (ΔS) decrease with decrease in concentration in both the solvent. These different results for all the tested ligands may be due to different polarity index of non-polar solvent xylene and cyclohexane.

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