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Measurement of Some Thermodynamic and Acoustical Properties of Substituted-P-Benzoquinones In N, N-Dimethylformamide At 303.15K

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Abstract: Density, viscosity and ultrasonic velocity of four substituted-p-benzoquinone in N,N-dimethylformamide (DMF) were measured at303.15K. From the experimental data, various thermodynamic and acoustical properties such as specific impedance (Z), adiabatic compressibility (β), intermolecular free length (L_f), apparent molar volume ($ø_v$), apparentmolar compressibility ($ø_k$), relaxationstrength (r),free volume(V_f),molarcompressibility(W),Rao's molar sound function(R_m),etc., have been computed. The validity of the data was tested by applying into Bachem's, Masson's, Gucker's relation and John-Doles equation. The results are explained in terms of possible molecularinteractions existing between the components of thesolutions.

Keywords: Benzoquinones; N, N-dimethylformamide;Acoustical properties;Molecularinteractions.

1. Introduction

Recently ultrasonic studies in aqueous solution of various drugs yield a piece of essential information about the strength of the intermolecular interactions and physical nature [1-2]. The interpretation of the nature of molecular interactions depends upon knowledge of the basics of different experimental aspects of the binary fluid system and the hypothetical analysis of ultrasonic velocity. The interpretation of the nature of molecular interactions depends upon knowledge of the basics of different experimental aspects of the binary fluid system and the hypothetical analysis of ultrasonic velocity. There is thus much practical use to study and understand the experimental aspects of certain aqueous electrolytic solution through the exposure of them to the ultrasound[3-4]. Extended applications can be found in the ultrasonic studies as the ultrasounic velocity in liquids and mixtures are closely related to several parameters which determine the physicochemical behavior of liquid and liquid soltions.Studies of intermolecular interactions play animportant role in understanding the interactions thattake place in solutions. Changes in density,

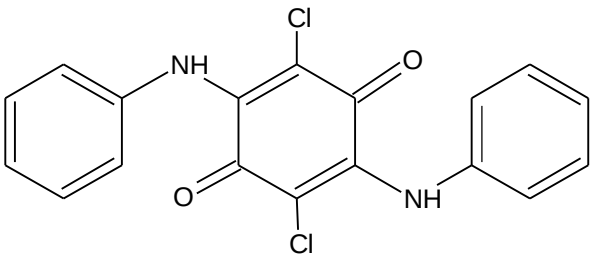
viscosity,ultrasound velocity and other parameters from temperatureand concentration have been considered bymany scientists and shed light on the structuralchanges occurring in solutions [5-6]. Quinones make up a large class of compound with diverse biological activity. They are widely used as anticancer, antibacterial, antimalarial drugs as well as fungicides [7-9]. A variety of 1, 4-benzoquinones and their nitrogen analogues have been reported for their antitumour activities [10-13]. Extensive investigation in the field of substituted-p-benzoquinones shows that much has been reported about their preparation and physical properties. However, very little is known about theiracoustical properties. A literature survey shows that there has been an increased interest in thermodynamic and transport properties of liquid solutions and in liquid mixtures [14-18]. The measurement of density, viscosity and ultrasonic velocity in the solution furnishes information about intermolecular interactions and geometrical effects [19-21].

These finding prompted us to study the molecular interaction of somesubstituted-p-benzoquinones in non-aqueous solution. Thus, in the present paper, we have synthesized somesubstituted-p-benzoquinones and measured the density, ultrasonic velocity and viscosity of these derivatives in dimethylformamide (DMF) solutions at 303.15K

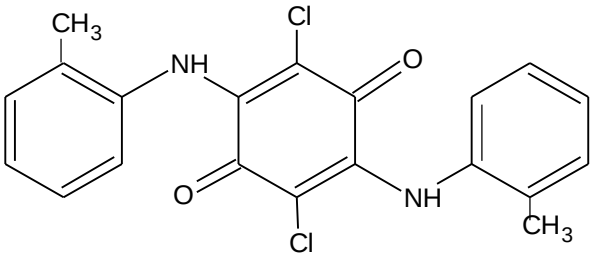
2. Experimental

The derivatives of substituted-p-benzoquinones are synthesized in our laboratory and purified. The structure of these compounds was confirmed by UV, IR, ^{1}H NMR. ^{13}C NMR, Mass and CHN analysis. The structures of these derivatives are shown in Scheme 1-4.

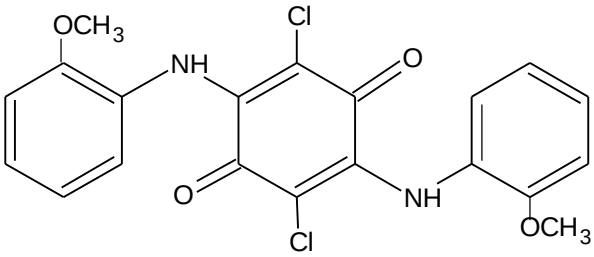
Schemes 1 to 4



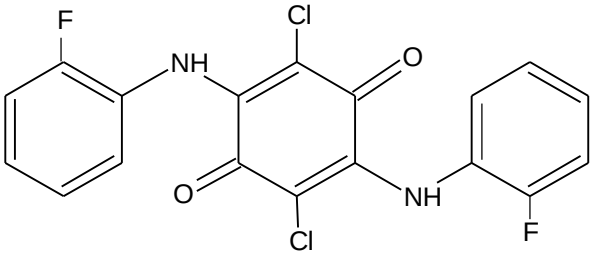
Scheme 1. SBQ I: 2, 5-Dianilino-3, 6-dichloro-1, 4-benzoquinone



Scheme 2. SBQ II: 2, 5-Bis (2'-methylanilino) -3, 6-dichloro-1, 4-benzoquinone



Scheme 3. SBQ III: 2, 5-Bis (2'-methoxyanilino) -3, 6-dichloro-1, 4-benzoquinone



Scheme 4. SBQ IV: 2, 5-Bis (2'-fluoroanilino) -3, 6-dichloro-1, 4-benzoquinone

The solvent dimethylformamide used was of laboratory grade and was purified prior to use by an appropriate method [22]. The estimated purity was better than 99.8%.

For each benzoquinone solutions of different concentrations (in molarity, C) were prepared. The density, ultrasonic velocity and viscosity of pure solvent and of solutions were measured at 303.15K by using a pyknometer, the multifrequency interferometer, operating at 2MHz and Ubbelhode viscometer with the uncertainties of 0.0001g/ml, ± 0.01% and ± 0.06% respectively. The temperature was regulated by water thermostat. The uncertainty of in temperature measurement is ± 0.1K and that of concentration measurement is 0.0001mol dm^{-3}.

3. Result and discussion

From the experimental data of density, ultrasonic velocity and viscosity, various acoustical properties such as specific impedance(Z), adiabatic compressibility (β), Rao's molar sound function(R_m), Vander Waal's constant (b), molar compressibility (W), intermolecular free length (L_f)relaxation strength(r),free volume (V_f), internal pressure (π),apparent molar volume($ø_v$), apparent molar compressibility($ø_k$) etc. have been evaluated by standard equations reported earlier given below.

(a) Specific impedance (Z) $Z = U\rho$ where U is ultrasonic velocity and the ρ density of solution

(b) Adiabatic compressibility (β) $\beta = 1/(U^2\rho)$

(c) Intermolecular free length $L_{f(\beta)}$ $L_{f(\beta)} = K\beta^{1/2}$ where K is the Jacobson constant (6.31×10^4 at 30^{0C})

(d) Rao's molar sound function (R_m) $R_m = (M/\rho)U^{1/3}$ where M is the molecular weight of the solution

(e) Vander Waals constant (b) $b = (M/\rho)(1-(RT/MU^2)(\sqrt{1+MU^2/3RT-1}))$ where R is gas constant and T absolute temperature

(f) Molar compressibility (W) $W=(M/\rho)\beta^{-1/7}$

(g) Internal pressure (π) $\pi = bRT(K\eta/U)^{1/2}(\rho^{2/3}/M^{7/6})$ where K is a constantand its value is 4.28×10^9, R the gas constant and η the viscosity of solution, b the packing fraction (2)

(i) Relaxation strength(r) $r = 1 – (U/U_\alpha)^2$ where $U_\alpha=1.6\times10^5$ cm^2/s

(j) Free volume (V_f) $V_f=(MU/K\eta)^{3/2}$

(k) Apparent molar volume ($ø_v$) $Ø_v = M/\rho-1000(\rho -\rho_o)/\rho C$ where $\rho_0$is density of pure solvent, C the concentration of solution

(l) Apparent molar compressibility ($ø_k$) $Ø_k = 1000\beta/C –\beta_o/\rho_o(1000\rho/C – M)$

Some of these parameters are given in Table 1.Few parameters were correlated with concentration and the correlation coefficients along with correlation equations are given in Table 2.From these equations, it is clear that excellent linear correlation between some parameters and concentrations were observed.

Table 1

Variation of acoustical parameters with concentration of benzoquinone derivatives in DMF at 303.15 K

Conc. (M)	Velocity,U ($\times 10^{-5}$cm/s)	Acoustic impedence,Z ($\times 10^{-5}$g cm^{-2})	Adiabatic compression,β ($\times 10^{11}$cm^2/dyn)	Intermolecular free length L_f (A^0)	Molar compress,W	Vander walls constants,b ($\times 10^{-4}$cm^{3}mol^{-1})	Free volume,Vf ($\times 10^9$cm^3)	Internal pressure,π
SBQ I								
0.000	1.4555	1.3699	5.0153	0.4469				
0.001	1.4591	1.3745	4.9863	0.4456	61.6985	111.3638	0.2430	490.9873
0.003	1.4666	1.3833	4.9292	0.4430	61.7574	111.8914	0.2528	493.7395
0.005	1.4709	1.3891	4.8942	0.4414	61.7777	112.1746	0.2577	494.8027
0.007	1.4750	1.3946	4.8613	0.4400	61.801	112.4542	0.2639	496.7477
0.009	1.4785	1.3995	4.8327	0.4387	61.8171	112.6881	0.2705	499.1118
0.011	1.4823	1.4045	4.8034	0.4373	61.8479	112.9685	0.2756	500.2732
0.013	1.4865	1.4098	4.7718	0.4359	61.8834	113.2794	0.2821	502.0516
0.015	1.4905	1.4154	4.7402	0.4344	61.8997	113.5392	0.2880	503.5339
SBQ II								
0.001	1.4662	1.3806	4.9402	0.4435	61.8066	111.9532	0.2403	485.4814
0.003	1.4692	1.3847	4.9154	0.4424	61.8280	112.1730	0.2432	485.9097
0.005	1.4800	1.3964	4.8388	0.4389	61.9372	112.9762	0.2516	486.0863
0.007	1.4875	1.4051	4.7845	0.4365	62.0008	113.5153	0.2579	486.4617
0.009	1.4950	1.4140	4.7306	0.4340	62.0584	114.0421	0.2645	486.9296
0.011	1.4999	1.4207	4.6928	0.4323	62.0737	114.3461	0.2694	487.6691
0.013	1.5062	1.4292	4.6453	0.4301	62.0886	114.7202	0.2753	488.4023
0.015	1.5135	1.4384	4.5933	0.4277	62.1262	115.1942	0.2828	489.4178
SBQ III								
0.001	1.4840	1.3954	4.8291	0.4385	62.0983	113.4820	0.2500	482.5746
0.003	1.4958	1.4077	4.7492	0.4348	62.2393	114.4131	0.2583	481.9902
0.005	1.5026	1.4156	4.7013	0.4327	62.3090	114.9376	0.2630	481.5085
0.007	1.5088	1.4231	4.6573	0.4306	62.3657	115.4041	0.2672	481.0367
0.009	1.5142	1.4294	4.6202	0.4289	62.4297	115.8461	0.2712	480.7161
0.011	1.5197	1.4360	4.5825	0.4271	62.4891	116.2836	0.2754	480.4765
0.013	1.5266	1.4437	4.5373	0.4250	62.5703	116.8407	0.2810	480.2583
0.015	1.5300	1.4485	4.5124	0.4239	62.5991	117.1053	0.2838	480.1712
SBQ IV								
0.001	1.4599	1.3760	4.9782	0.4452	61.6832	111.3743	0.2373	486.8721
0.003	1.4652	1.3834	4.9334	0.4432	61.6940	111.6918	0.2410	486.8814
0.005	1.4843	1.4041	4.7981	0.4371	61.8639	113.0482	0.2528	485.4074
0.007	1.4954	1.4175	4.7176	0.4334	61.9314	113.7816	0.2597	484.6117
0.009	1.5066	1.4299	4.6419	0.4299	62.0386	114.6059	0.2667	483.5118
0.011	1.5181	1.4428	4.5655	0.4264	62.1429	115.4406	0.2739	482.3811
0.013	1.5297	1.4555	4.4914	0.4229	62.2588	116.3068	0.2816	481.3348
0.015	1.5385	1.4660	4.4336	0.4202	62.3247	116.9231	0.2874	480.5348

Table 2

The correlation coefficients (γ) and correlation equations between some acoustical parameters and concentrations (C) of benzoquinone derivatives in DMF solutions at 303.15 K

Parameters	γ	Correlation equation	Parameters	γ	Correlation equation
SBQ I			**SBQ II**		
U(cm s^{-1})	0.9944	U-276310C=145746	U(cm s^{-1})	0.9927	U-392200C=146070
Z(g cm^{-2})	0.9968	Z-350023C=137207	Z(g cm^{-2})	0.9938	Z-421289C=137488
η(cP)	0.9964	η-0.0469C=0.0078	η(cP)	0.9975	η-0.0224C=0.0077
r	0.9945	r+3.1534C=0.1702	r	0.9928	r+4.4910C=0.1666
W	0.9812	W-16.8120C=61.6940	W	0.9830	W-59.4310C=61.6790
V_f(cm^3)	0.9969	V_f -4×10^{-9}C=3×10^{-10}	V_f(cm^3)	0.9954	V_f -3×10^{-9}C=2×10^{-10}
b	0.9937	b-2×10^6C=1×10^6	b	0.9935	b-40659C=14362
π	0.9951	π-105016C=490.15	π	0.9963	π-220.27C=485.56
L_f	0.9957	L_f $_{(β)}$+0.9867C=0.4462	L_f	0.9943	L_f $_{(β)}$+1.2736C=0.4453
SBQ III			**SBQ IV**		
U(cm s^{-1})	0.9947	U-463512C=148091	U(cm s^{-1})	0.9939	U-666250C=145060
Z(g cm^{-2})	0.9969	Z-508359C=139169	Z(g cm^{-2})	0.9955	Z-773318C=136573
η(cP)	0.9887	η-0.0146C=0.0077	η(cP)	0.9947	η-0.018C=0.0077
r	0.9948	r+5.3952C=0.1434	r	0.9940	r+7.6007C=0.1781
W	0.9903	W-50.499C=62.07	W	0.9879	W-45.876C=61.608
V_f(cm^3)	0.9946	V_f -4×10^{-9}C=2×10^{-10}	V_f(cm^3)	0.9946	V_f -4×10^{-9}C=2×10^{-10}
b	0.9931	b-4×10^6C=1×10^6	b	0.9931	b-4×10^6C=1×10^6
π	0.9997	π+332.76C=482.9	π	0.9886	π+396.41C=487.61
L_f	0.9958	L_f $_{(β)}$+1.4715C=0.4395	L_f	0.9944	L_f $_{(β)}$+2.2602C=0.4482

The ultrasonic velocity increases continuously with concentration for all the four benzoquinone systems SBQ I to SBQ IV (Scheme 1 to Scheme 4).Ultrasonic velocity depends on intermolecular free length (L_f).With the decrease of free length, velocity increases or vise versa. It is observed that L_f decreases linearly for all the four benzoquinone systems. Rao molar sound function (R_m), molar compressibility (W) and Van der Waal'sconstant (b) increases linearly for all the four benzoquinone systemssuggesting thereby absence of complex formation. Relaxation strength(r) and intermolecular free length (L_f) are observed to decrease while specific impedance (Z) is

observed to increase with concentration for SBQ I to SBQ IV. Decrease in r and $L_f$and increase in Z, suggests presence of solute-solvent interactions in all the four benzoquinone systems. This is further confirmed by viscosity values. As shown in Fig. 1, viscosity increases with increase of concentration of benzoquinones in all the four systems, suggesting thereby more association between solute-solvent molecules in all the SBQ (I – IV) systems.

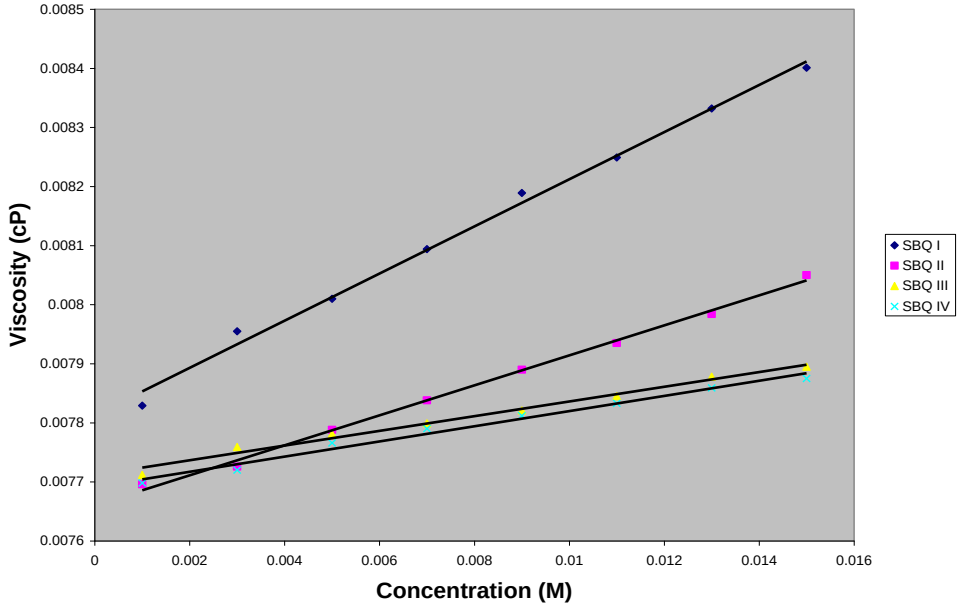


Fig. 1. Variation of viscosity with concentration in the four derivatives

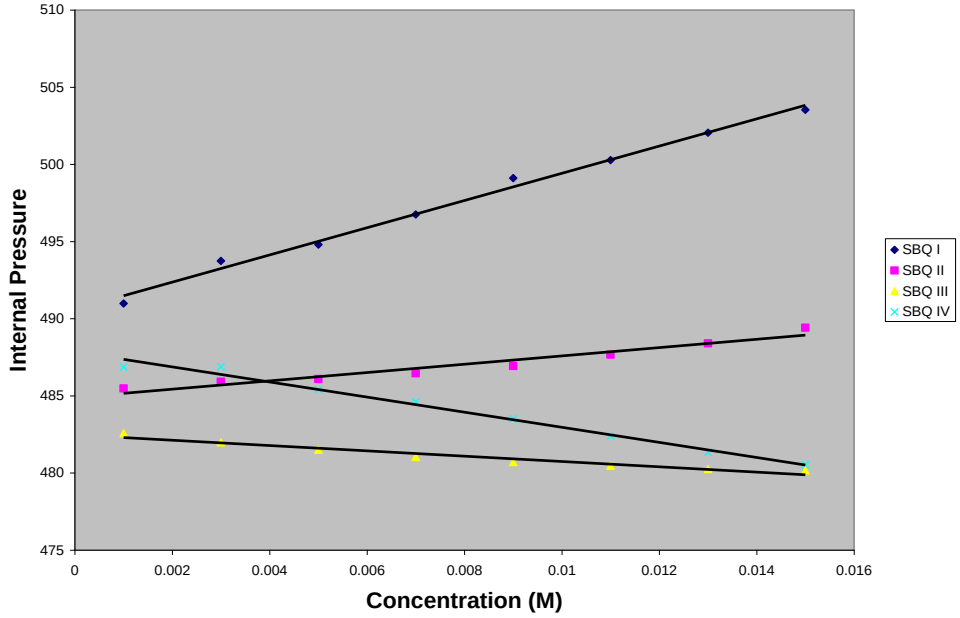


Fig. 2. Variation of internal pressure with concentration in the four derivatives

As shown in Fig.2, internal pressure values are observed to increase in SBQ I and SBQ II. However, internal pressure values are observed to decrease in SBQ III and IV. Theincrease in the internal pressure with concentration suggests the increase in cohesive forces between solute-solvent molecule and vise versa. Therefore, decrease in internal pressure in SBQ III and SBQ IV suggests presence of solute-solvent interaction. The free volume (V_f) values are observed to increase with concentration in all the four benzoquinone systems suggesting close association between solute and solvent molecules.

Further, the adiabatic compressibility, apparent molar volume, apparent molar compressibility and viscosity data were fitted to Bachem's [23], Masson's [24], Gucker's relation [25] and John-Doles equation [26] respectively.

$$\beta = \beta_0 + AC + BC^{3/2}$$

$$Ø_v = Ø_v^o + Sv\sqrt{C}$$

$$Ø_k = Ø_k^o + S_k\sqrt{C}$$

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

It is found that the relations are applicable above 0.003M concentrations. A and B constants of John-Dole's and Bachem's equation along with Masson's constants ($Ø_v^o$ and Sv) and Gucker's constants ($Ø_k^o$ and S_k) are reported in Table 3.

Table 3

Values of various constants obtained from different relation for benzoquinone derivatives in DMF at 303.15K

S No.	Bachem's relation		Messon's relation		Gucker's relation		John Dole's eqn.	
	A	B	$ø_v^o$	S_v	$ø_k^o$	S_k	A	B
SBQ I	-5×10^{-10}	2×10^{-9}	-443.13	1938.40	-4×10^{-7}	2×10^{-6}	0.7350	3.2046
SBQ II	-5×10^{-10}	1×10^{-9}	-25.02	656.58	-3×10^{-7}	2×10^{-6}	0.1354	5.5681
SBQ III	-2×10^{-9}	3×10^{-8}	1091.80	-14809	-3×10^{-6}	5×10^{-5}	0.3152	-2.9612
SBQ IV	3×10^{-10}	-2×10^{-8}	-739.15	12969	3×10^{-7}	-2×10^{-5}	0.0518	1.8844

It is evident from Table 3 that value of Bachem's constant A and B in SBQ IV are positive and negative respectively in comparison to the other three benzoquinone systems. The positive value of A and negative value of B supports the existence of solute-solute interaction with solute-solvent interaction in SBQ IV. This is further supported by the value of Gucker's constant $Ø_k^o$ and S_k in SBQ IV, which are positive and negative

respectively in comparison to the remaining three systems. The positive value of $Ø_k^o$ and negative value of S_k are indicative of the loose attachment of the solvent molecule to the solute molecules. In case of SBQ III the existence of solute-solute interaction is supported by the value s of Masson's constants $Ø_v^o$ and Sv,which are positive and negative in comparison to the other three SBQ systems. The positive value of $Ø_v$ indicates loose attachment of solvent molecules to the ions and negative$Ø_v$ implies electrostatic solvations of ions [27-28]. The solute-solute interaction in SBQ III is further supported by negative value of B parameter of John-Doles equation. The existences of solute-solute interaction in SBQ III & IV are also supported by the internal pressure value which decreases with concentration.

4.Conclusion

In all the benzoquinone systems (SBQ I to SBQ IV) in DMF at 303.15solute-solvent interactions exist. However, in SBQ III and SBQ IVsolute-solute interactions are also presents along with solute-solvent interactions.

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