Comparative Acoustic Studies of Some Thiosemicarbazide and Thiaoxadizine at Different Composition

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ABSTRACT

The experimental data of ultrasonic velocity, density, viscosity has been obtained for some thiosemicarbazide and thiaoxadizenes at different temperature in 70% and 75% DMF over the conc. range of (0.002 to 0.01) mol Kg^{-1}. The derived parameters such as apparent molar volume of solute (Φv), limiting apparent molar volume of solute ($\Phi^0 v$), limiting apparent molar expansivity ($\Phi^0 E$), thermal expansion coefficient (α^*) and Jones-Dole viscosity coefficient were obtained using the density and viscosity results. The variations of these properties with concentration give the information about solute-solvent interactions.

Keywords: Density, Relative Viscosity, Apparent Molar Volume, Limiting Apparent Molar Volume, Molar Expansivity.

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INTRODUCTION

In recent years, the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to molecular interaction and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixture [1-3] and in pure liquids [4-8].The variation of ultrasonic velocity and related parameters throw light on the structural changes associated with the liquid mixture having weakly interacting components [9-10] as well as strongly interacting components. The interaction of drugs is of significant importance. Over many years studies of thermodynamic and

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transport properties of model compounds such as alkali halides, tetra alkyl ammonium halides, hydrocarbons, alcohols and amines have witnessed the importance of solute-solvent interactions [11-16]. Therefore, it was thought worthwhile to undertake thermodynamic and acoustic studies of the compounds viz., 1-γ-picolinoyl-4-phenyl thiosemicarbazide(C1), 1-γ-picolinoyl-4-m-tolyl thiosemicarbazide(C2), 3-(pyrid-4yl)-5H-6-m-tolyl imino-1,2,4,5-thiaoxadiazine(R1),3-(pyrid-4yl)-5H-6-O-tolylimino-1,2,4,5-thiaoxadiazine(R2) in 70% and 75% DMF media. We report here in this communication densities, Relative Viscosities of (C1+70%DMF), (C2+70%DMF), (R1+70%DMF), (R2+70%DMF), (C1+75%DMF), (C2+75%DMF), (R1+75%DMF), (R2+75%DMF) at T= (283,288,293,298 and 303) K over the concentration range, (0.002 to 0.01) mol Kg^{-1}. From density measurements, the apparent molar volume (Φv), limiting apparent molar volume of solute ($\Phi^0 v$), limiting apparent molar expansivity ($\Phi^0 E$) thermal expansion coefficient ($\alpha^{*)}$) and the temperature coefficient of apparent molar thermal expansivity ($d^2\Phi^0 v/dT^2$) have been computed and using density and viscosity data, the Jones-Dole equation viscosity A, B coefficients have been obtained. The results of all these parameters are presented and discussed below. Literature survey on ultrasound velocity measurements shows that very little work has been carried out for thiosemicarbazides and thiaoxadizines. Thus, in the present paper we have used this technique for better understanding of molecular interactions in these compounds, since the compounds pursue biological importance.

MATERIALS AND METHODS

The solutes used in the present investigation were synthesized by standard methods as reported by the earlier workers [17]. They are 1-γ-picolinoyl-4-phenyl thiosemicarbazide(C1), 1-γ-picolinoyl-4-m-tolyl thiosemicarbazide(C2), 3-(pyrid-4yl)-5H-6-m-tolyl imino-1,2,4,5-thiaoxadiazine(R1) and 3-(pyrid-4yl)-5H-6-O-tolylimino-1,2,4,5-thiaoxadiazine(R2). The above compounds were dried in a vacuum oven and then stored in desiccators under vacuum over fused calcium chloride before use. Afterwards, they were used without any further purification. All the solutions were freshly prepared in double distilled DMF on a molality basis. Densities, viscosities, and velocities were measured at 283 K, 288 K, 293 K, 298 K and 303 K. Temperature of the experimental water bath was maintained constant up to $\pm 0.01^0$C by circulating the coolant liquid from the LTB-10.

The densities of the solutions were measured at different temperature by the hydrostatic plunger method. A monopan balance of least count 0.0001g was used to record change in plunger weight dipped in solutions.

The viscosities of the solutions were measured by using the Ostwald Viscometer. The viscometer was suspended in an experimental bath having a glass window to observe the meniscus of the liquid. To determine the flow time of DMF, the viscometer was cleaned thoroughly with double distilled DMF, dried and then filled with a fixed amount of 70% and 75% DMF and mounted inside the thermostat vertically. It was kept in an experimental bath for (15 to 20) min to acquire the thermal equilibrium. The liquid was then allowed to flow down through the capillary. The stop watch was started as soon the liquid meniscus touched the upper fiducial mark, the stop-watch having an uncertainty of $\pm$ 0.1s was used to measure the flow for given solution, the viscometer was rinsed with given solution and same amount of the solution was introduced in the viscometer and flow time was measured between same two marks on the capillary. On average,

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three readings were taken. Ultrasonic velocity measurements were made by variable path single crystal interferometer (Mittal Enterprises, Model F – 81S) at 2 MHz with accuracy of $\pm$ 0.03%.

RESULTS AND DISCUSSION

Table 1:**Free Length(Lf),relative association(Ra) and Apparent molar volume(φv) of 3-(pyrid-4yl)-5H-6-m-tolyl imino-1,2,4,5-thiaoxadiazine(R1),3-(pyrid-4yl)-5H-6-O-tolylimino-1,2,4,5-thiaoxadiazine(R2)**

70%DMF						
T=283 K		R1			R2	
$m/(mol.Kg^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.09598	0.96777	83912	0.89418	0.95944	-84282
0.004	1.09662	0.98159	41829	0.90105	0.96438	-90807
0.006	1.09824	0.98519	32520	0.93780	0.97785	-92179
0.008	1.09928	0.98783	25654	1.02633	1.00805	-93062
0.01	1.10084	0.98876	24285	1.07497	1.02487	-95837
T=288 K		R1			R2	
$m/(mol.Kg^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.09824	0.98951	17228	1.09564	1.02724	-101974
0.004	1.09941	0.98992	17018	1.09892	1.02847	-102532
0.006	1.11251	0.99392	16760	1.10235	1.02963	-102810
0.008	1.11510	0.99565	13604	1.11257	1.03291	-103089
0.01	1.11744	0.99739	10222	1.11622	1.02667	-103967
T=293 K		R1			R2	
$m/(mol.Kg^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.11006	0.99138	15408	1.13289	1.02866	-113932
0.004	1.11363	0.99287	13771	1.13310	1.02886	-114385
0.006	1.12136	0.99542	12817	1.14311	1.03191	-114460
0.008	1.11280	0.99786	11047	1.15131	1.03494	-116297
0.01	1.14188	1.00208	10448	1.15188	1.03679	-119788
T=298 K		R1			R2	
$m/(mol.Kg^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.11380	0.98597	19344	1.23394	1.05913	-141498
0.004	1.13571	0.99294	16909	1.24414	1.06267	-143815
0.006	1.1516	0.99972	7322	1.24661	1.06856	-162600
0.008	1.15358	1.00102	4135.6	1.25098	1.07904	-192049
0.01	1.15914	1.01966	-6787.5	1.25745	1.09427	-240204
T=303 K		R1			R2	
$m/(mol.Kg^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.13417	1.0208	-120294	1.26166	1.06798	-163261
0.004	1.14175	1.033	-163327	1.26847	1.07064	-166293
0.006	1.14606	1.08061	-342521	1.27449	1.0732	-169846
0.008	1.14802	1.08998	-372927	1.27622	1.07451	-173196
0.01	1.23178	0.94939	260106	1.21755	1.095199	-389028

T=283 K		C1			C2	
$m/(mol.Kg^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.06726	1.118	291662	0.97344	1.0135	-148265
0.004	1.06457	1.116	-290098	0.97298	1.0128	-147051
0.006	1.06335	1.115	-288830	0.97243	1.0126	-146978
0.008	1.06214	1.114	-287685	0.97212	1.0119	-1455580
0.01	1.06015	1.11	-282238	0.96772	1.01	-144635
T=288 K		C1			C2	
$m/(mol.Kg^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.12471	1.222	-472120	1.01082	1.0267	-173732
0.004	1.11377	1.216	-469442	0.99361	1.0197	-170634
0.006	1.11218	1.215	469338	0.98273	1.0157	-170079
0.008	1.10736	1.164	-393019	0.98200	1.0153	-169627
0.01	1.09721	1.13	-338211	0.97927	1.0141	-168845
T=293 K		C1			C2	
$m/(mol.Kg^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.14817	1.23	-555263	1.10573	1.054	-199896
0.004	1.14741	1.229	-554349	1.09963	1.0517	-198984

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0.006	1.14650	1.228	-552588	1.09892	1.0511	-197639
0.008	1.14433	1.338	-697386	1.08743	1.0466	-195282
0.01	1.14049	1.225	-551264	1.07667	1.0428	-194175

T=298 K		C1			C2	
m/(mol.Kg⁻¹)	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.16475	1.342	-821873	1.10573	1.054	-199896
0.004	1.16439	1.339	-818715	1.09963	1.0517	-198984
0.006	1.16301	1.333	-811650	1.09892	1.0511	-197639
0.008	1.15799	1.22	-638710	1.08743	1.0466	-195282
0.01	1.15685	1.379	-866751	1.07667	1.0428	-194175

T=303 K		C1			C2	
m/(mol.Kg⁻¹)	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.18542	2.404	-1000000	1.19483	1.1311	-457791
0.004	1.18356	1.392	-971475	1.15167	1.1112	-438691
0.006	1.17220	1.387	-971060	1.15516	1.1108	-437329
0.008	1.17154	1.385	-969221	1.14306	1.1052	-428481
0.01	1.16885	1.329	-899640	1.13719	1.1006	-419898

			75%DMF			
T=283 K		**R1**			**R2**	
m/(mol.Kg⁻¹)	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.11405	0.92916	227104	1.00298	0.89146	255635.5
0.004	1.10492	0.92556	232133	1.00031	0.88869	265699.7
0.006	1.10417	0.92447	236374	0.99928	0.88718	271847.2
0.008	1.14064	0.93308	243342	0.99882	0.88578	278364.5
0.01	1.13712	0.9321	243406	0.99770	0.88160	298326.2
T=288 K		**R1**			**R2**	
m/(mol.Kg⁻¹)	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.15383	0.97763	86852	1.14583	0.95155	202221.8
0.004	1.14261	0.94899	210749	1.14377	0.95069	203699.8
0.006	1.14098	0.94596	224056	1.13718	0.94849	205601.3
0.008	1.13604	0.94238	235578	1.11604	0.93695	234901.2
0.01	1.12562	0.93909	237717	1.11009	0.93447	239144.9
T=293 K		**R1**			**R2**	
m/(mol.Kg⁻¹)	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.17313	0.99341	35039	1.16655	0.99113	36934.9
0.004	1.17090	0.99042	45788	1.16097	0.98658	50517.3
0.006	1.16698	0.99442	22693	1.15711	0.98506	52459.3
0.008	1.16670	0.99417	23433	1.15266	0.98274	57338.8
0.01	1.16358	0.99281	25554	1.15003	0.98016	65894.1
T=298 K		**R1**			**R2**	
m/(mol.Kg⁻¹)	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.1894	1.01401	-44909	1.17482	1.00905	-40981.3
0.004	1.18932	1.01373	-43651	1.17446	1.00649	-28776
0.006	1.18286	1.01068	-37696	1.17367	1.00582	-26550.5
0.008	1.18141	1.00872	-30003	1.17245	1.00430	-20708.6
0.01	1.17590	1.00172	-2636	1.17044	1.00228	-13387.1
T=303 K		**R1**			**R2**	
m/(mol.Kg⁻¹)	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.24885	0.95634	245433	1.31297	1.23190	-667315.7
0.004	1.24689	0.95538	248019	1.23855	1.19400	-636475.4
0.006	1.23492	0.95203	249605	1.23078	1.18911	-631096.4
0.008	1.23423	0.9504	257969	1.22864	1.18651	-626779.1
0.01	1.2317	0.94939	260106	1.21755	1.09519	-389028.5

			75%DMF			
T=283 K		C1			C2	
m/(mol.Kg⁻¹)	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.10355	0.94693	132618	1.12301	0.93352	218251.9
0.004	1.10536	0.95053	119221	1.14814	0.94179	211926.5
0.006	1.10855	0.95563	101371	1.14882	0.94434	200993.2
0.008	1.10893	0.95614	99660	1.15234	0.94655	195279.7
0.01	1.11126	0.96078	83017	1.15684	0.99522	-1368.1
T=288 K		C1			C2	
m/(mol.Kg⁻¹)	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$	$Lf/(A^0)$	R_A	$\Phi v/(m^3.mol^{-1})$
0.002	1.10727	0.96465	85243	1.13962	0.99686	-15737.9

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m/(mol.Kg⁻¹)	Lf/(A⁰)	R_A	Φv/(m³.mol⁻¹)	Lf/(A⁰)	R_A	Φv/(m³.mol⁻¹)
0.004	1.10939	0.96844	70513	1.14418	0.99825	-15993.9
0.006	1.10939	0.97315	49075	1.14947	1.00008	-17241.3
0.008	1.10984	0.97539	39630	1.15244	1.00231	-22957.1
0.01	1.12748	0.98083	38317	1.15481	1.00343	-24773.9
T=293 K	C1			C2		
m/(mol.Kg⁻¹)	Lf/(A⁰)	R_A	Φv/(m³.mol⁻¹)	Lf/(A⁰)	R_A	Φv/(m³.mol⁻¹)
0.002	1.12835	0.9864	8808	1.16076	1.00723	-40901.9
0.004	1.12982	0.98848	1465	1.16146	1.00833	-44721.1
0.006	1.13115	0.99314	-17345	1.16358	1.00895	-44721.1
0.008	1.13276	0.99462	-21735	1.16698	1.01026	-46123
0.01	1.13363	0.99563	-25029	1.16997	1.01112	-46123
T=298 K	C1			C2		
m/(mol.Kg⁻¹)	Lf/(A⁰)	R_A	Φv/(m³.mol⁻¹)	Lf/(A⁰)	R_A	Φv/(m³.mol⁻¹)
0.002	1.14084	1.00386	-63926	1.17159	1.03965	-187722.9
0.004	1.14158	1.00995	-92344	1.17202	1.05692	-260185.9
0.006	1.15807	1.01492	-92979	1.173311	1.06206	-279413.4
0.008	1.15940	1.0182	-106649	1.175903	1.06455	-286226.2
0.01	1.15975	1.02027	-115916	1.176624	1.06478	-286260.4
303K	C1			C2		
m/(mol.Kg⁻¹)	Lf/(A⁰)	R_A	Φv/(m³.mol⁻¹)	Lf/(A⁰)	R_A	Φv/(m³.mol⁻¹)
0.002	1.20775	0.95609	187248	1.226671	0.99902	-5113.8
0.004	1.21196	0.95796	183086	1.230938	1.00720	-37580.3
0.006	1.17964	2.06626	130560	1.234773	1.00976	-44435.4
0.008	1.22485	0.97271	122497	1.255105	1.01651	-50008.5
0.01	1.22864	0.97437	119112	1.285221	1.02722	-61667.2

Table2: Limiting Apparent molar volume, solute-solvent interaction, limiting apparent expansibility, B,A

	70% DMF								
T	Φ⁰V(m³.mol⁻¹)	S_v	ΔΦ⁰V	Δ T	Φ⁰E/(m³.mol⁻¹.K⁻¹)	α	last	B/(dm³.mol⁻¹)	A/(dm³.mol⁻¹)	dB/dT
					C1					
283	-299265	148893.6						0.79547	-0.00635	0.0548
288	-605363	2359987	-205328	10	-20532.7			0.54800	-0.02680	-0.04944
293	-504593	-1034714				0.102179	-6205.18	0.30108	-0.01379	-0.03599
298	-851508	799855.6	-825846	10	-82584.5			0.18806	-0.01068	-0.01299
303	-1330439	4411153						0.17113	-0.00530	-0.01881
					C2					
283	-151197	62627.86						-0.18662	0.00290	0.02275
288	-176695	81521.06	-54103.4	10	-5410.3			0.22757	-0.02941	0.02895
293	-205300	108114.8				0.081027	-2244.91	0.10293	-0.01845	-0.00522
298	-237177	96827.11	-278595	10	-27859.4			0.17534	-0.01656	0.01772
303	-483895	632983.5						0.28018	-0.01739	-0.01753
					R1					
283	119571	-1039444						-0.25868	0.00381	-0.03754
288	23928	-119532	-99969.3	10	-9996.9			-0.3753	0.01125	-0.0092
293	19601	-92077.7				0.066322	2259.392	-0.35065	0.01149	0.01063
298	91104	-1268938	125969.9	10	12596.9			-0.26905	0.01268	0.02225
303	145571	-5680007						-0.12807	0.01083	0.02690
					R2					
283	-77014	-189651						-0.32584	0.00643	-0.02909
288	-100439	-32472.9	-31762	10	-3176.2			-0.29086	0.00513	0.01623
293	-108776	-93308.8				0.034661	-118.816	-0.16348	0.00470	0.01204
298	-48336	-1703216	-43643	10	-4364.3			-0.17043	0.00492	-0.00617
303	-152420	-229909						-0.22516	0.01328	0.01704
	75%DMF									
T	Φ⁰V(m³.mol⁻¹)	S_v	ΔΦ⁰V	Δ T	Φ⁰E/(m³.mol⁻¹.K⁻¹)	α	last	B/(dm³.mol⁻¹)	A/(dm³.mol⁻¹)	dB/dT
					C1					
283	212452	320380						0.76246	-0.00873	0.08714
288	8433	254165	-159708	10	-15970.8			0.87147	-0.02906	-0.02937
293	52744	-296667				0.017874	3382.712	0.46878	-0.01147	-0.04155
298	-82304	673907	178562.9	10	17856.2			0.45595	-0.01120	0.00508
303	231307	279031						0.51964	-0.03088	-0.0456

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C2										
283	221758.5	696457						0.47400	-0.010538	0.03166
288	162189.6	732578	-204715	10	-20471.5			0.31660	-0.006737	-0.01506
293	17043.4	474639				-3.22692	-6905.26	0.32339	-0.017125	-0.01537
298	-60770.8	462696	-895242	10	-89524.1			0.16294	-0.00243	-0.00178
303	-878198.1	3842127						0.30559	-0.006493	-0.01629
R1										
283	172026.0	-864943						0.16662	0.01717	0.02420
288	125866.7	-924462	-132628	10	-13262.8			0.24204	0.01016	0.00878
293	39397.6	-669097				0.107458	3499.286	0.25448	0.01082	0.00706
298	-28745.2	-875210	217300	10	21730.0			0.31267	0.01923	-0.01126
303	256697.8	-1E+06						0.14185	0.02180	-0.03127
R2										
283	394431.1	-3E+06						-0.01023	0.01810	-0.01108
288	-6229.5	-174879	-432186	10	-43218.5			-0.11077	0.01208	-0.00646
293	-37754.8	-90208				0.481634	5006.92	-0.07487	0.00418	0.016724
298	-130587.8	-2E+06	68506.0	10	6850.6			0.05645	0.00344	-0.02413
303	30751.2	-940491						-0.31617	0.01019	-0.00565

The variation of Lf, R_A & Φv along with conc. at different temperature are shown in table-1 and table-2. From this, it is found that the decrease in free length with increase in concentration of linear molecules indicates that there is a significant interaction between solute and solvent molecules, suggesting a structure promoting behavior on addition of solute. The increase in temperature, however, makes the free length to increase as expected due to thermal expansion of the liquids [18].

The variation of relative association in the systems of cyclic molecules indicates the presence of molecular association between solute and solvent with addition of solute, which is in accordance with that reported by Jahagirdar and Shankarwar [19]. It has also been observed from the table that Φv varies linearly with concentration at all temperature. It is dependent on size and geometrical arrangement of solute in solution. A marked observation has been made that apparent molar volume increases with decrease in concentration of solute for the cyclic forms at all temperature indicating the decrease in stacking interaction between solute and solvent [20].

In table-3 are listed the values of slopes (Sv) for all systems at different temperature. It is observed from the above table that for C1,C2 systems; the values of Sv are positive, except that for C1 at 293K;while that for R1,R2, the value of Sv are negative, which can be due to cyclisation of molecular structure resulting in weak ion-ion interaction. For R1, R2 the value of Sv becomes more and more negative with rise in temperature. However in case of C1, C2, the value of Sv varies non linearly, but it is positive with increase or decrease of temperature.

In table-3 are also listed the values of limiting apparent molar volume of solutes (`$\Phi^0 v$) at different temperature, showing non-linear variation.

Romeo [21] observed that from the sign of $d^2\Phi^0 v/dT^2$; it can be decided whether the particular solute when dissolved in solvent, will act as structure maker or structure breaker. It has been observed that, except R1 having positive value of $d^2\Phi^0 v/dT^2$ is acting as structure breakers. Also C1 is a structure breaker and solute follows this order at low temperature; R1>R2>C2> C1.

It has been shown by Romeo et.al [22] that the coefficient of thermal expansion (α^*) can be used to interpret the solute-solvent interactions; which increases in the order R2<R1<C2<C1.

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The structure of solute plays an important role in deciding the values of α*.The largest value suggests higher value of expansivity. The data of $d^2\Phi v/dT^2$ matches with that obtained from α*; but R1, R2 and C2 slightly deviate the order.

It has been observed that B values decreases with temperature. These values are listed in table-3.Recently, it has been emphasized by a number of workers that dB/dT is a better criterion for determining the structure making or breaking tendency of any solute. The positive sign for dB/dT are structure breakers and those having negative sign are structure makers [23]. C1 is behaving as structure breaker at high temperature. The same trend is observed in C2 and R2 which can be due to addition effect of $-CH_3$ group with slight deviation in the value at T=298 K.For all the solute as the percentage of solvent increases Lf increases may be due to decrease in water content less number of molecules are available for making Hydrogen bond with DMF molecule, thereby affecting the other parameters.

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