Studies on Thermodynamic and Transport Properties of Curcumin Mixture at Different Temperatures

Archana Pandey, Anil kumar Shukla, A.R. Saksena and Roli Srivastava

Department of Chemistry, C.M.P. College University of Allahabad,
Allahabad 211002, U.P. India

Abstract: The physical properties i.e. density, viscosity and electrical conductance have been measured for the mixtures at 303.15, 308.15, 313.15, 318.15 and 323.15 K. The experimental data is used for the evaluation of various thermodynamic and acoustical parameters by which molecular interactions in solutions are interpreted. From the experimental data viscous relaxation time (τ), Gibbs's free energy (ΔG), classical absorption coefficient $(\alpha/f^2)_{cl}$, Falkenhagen coefficient (A), Jones-Doles coefficient (B) and thermodynamic parameters have been computed. Viscosities of the binary mixtures have been correlated successfully using Jones-Doles, Vand's, Moullik, Grunberg, Tamura-Kurata and Hind equation. The excess values of some of the above parameters have also been evaluated and discussed by Redlich Kister equation.in the light of molecular interactions in the mixture.

Key words: Molecular interactions · Density · Viscosity · Falkenhagen coefficient · Jones-Doles coefficient · Thermodynamic parameter

INTRODUCTION

Curcumin is a natural polyphenolic component of turmeric, the powderd rhizome of the perennial herb Curcuma Longa Linn (family-Zingiberacae), which is widely used as a dietary spice, as a colorant in cooking as well as herbal medicine in Ayurveda for centuries. Curcumin is the principal curcuminoid found in turmeric, along with minor amounts of demethoxy curcumin and bis demethoxy curcumin analogues. Chemically curcumin is (1,7- bis - 4-hydroxy-3- methoxyphenyl - 1,6- heptadiene-3,5- dione) known as diferyloylmethane [1] contains two parahydroxyl groups responsible for antioxidant activity, two keto groups and two double bonds responsible for anti-inflammatory, anticancer & antimutagen activity, two methoxy groups and an active methylene group established by analysis of chemical structure of curcumin via its biological activity. [2] Although curcumin is wonder drug but the main problems associated is due to its low solubility, poor adsorption and less bioavailability. An ideal drug has to act both as lipophilic (fat soluble) to pass through cell lining of the gut wall and also as water soluble in order to dissolve in the gut and blood serum. Due to its fat soluble nature and low molecular weight,

it is difficult for the molecules to squeeze through small gaps between the cells of gut wall. It has to pass from the gastrointestinal tract into the blood supplied by travelling through the cell lining of gut wall. The phospolipid bilayer of the gut and blood cells must be preventing it from entering and leaving the cell because curcumin is a polar molecule. Extensive investigations over last five decades have indicated that curcumin is a potent antioxidant [3-4] which are important for naturally occurring nutrients in maintaining health by slowing the destructive ageing process of cellular molecules. Those are found naturally in body & in plants such as fruits and vegetables and are used in diabetes [5-6], leishmanisis [7], psoriasis [8], apoptosis [9] and many other chronic diseases. The characteristics of living organisms such as selective permeability across cell membrane, muscle contraction, hearing and memory process and nerve conduction etc. can be interpreted in terms of interactions of molecules.

In some recent publications, efforts have been made to correlate biological activity with calculated physical parameters with the help of density, viscosity [10-11] and conductance [12-13] for mixtures at different temperatures. These antioxidants are important food additives and have many applications in the pharmaceutical industries.

Corresponding Author: Roli Srivastava, Department of Chemistry C.M.P. College University of Allahabad,
Allahabad 211002, U.P. India.

In solution of ionic solute the attraction between the solute and solvent is essentially of ion-dipole interaction depends mainly on ion size and polarity of the solvent. The strength of ion-dipole attraction in directly proportional to the size of the ion, charge and the magnitude of the dipole, but inversely proportional to the distance between the ion and the dipolar molecule. The dissolution of electrolyte in a solvent causes a volume contraction due to interaction between ions and solvent molecules and this may influence other acoustical properties of solution. In recent years, the studies of acoustical properties [14-16] of aqueous mixed electrolytic solutions have been found to be useful in understanding the specific ion-ion and ion-solvent interactions.

Ionic association and electrostatic interactions are the prime factors that must be considered in these electrolytes. Various types of interactions exist between the ions in the solutions and of these, ion-ion, ion-solvent interactions are of current interest. The interaction help in better understanding of the types of solute and solvent, i.e. whether the added solute modifies or distorts the structure of the solvent. The addition of organic solvent to an aqueous solution of electrolyte brings about the change in ion salvation [17] that often results in a large change in the reactivity of dissolved electrolyte.

When curcumin is taken orally, 75% of it is excreted in the faces while only traces appear in urine [18]. Invitro studies were carried out to access degradation kinetics of curcumin under various pH conditions and the stability of curcumin in physiological matrices was investigated [19] suggests that curcumin has very low bioavailability. Curcumin shows lots of pharmacological activities but it is a very good antioxidant. It helps in maintaining health by scavenging the free radicals, although free radicals help in the proper functioning of immune system but when the free radicals increase abnormally, the danger begins. Curcumin having antioxidant property breaks the free radical chain reaction. Antioxidants are chosen for the molecular interaction studies because they have great potential and are gaining popularity. This type of work with therapeutic active antioxidant curcumin has been reported so far the first time.

MATERIALS AND METHODS

Curcumin was purchased from Central Drug House (P) Ltd. Bombay-New Delhi and purified by preparative T. L. C. Using Silica- gel G. dried in vacuum desiccators over Silica gel. Methanol, Sodium chloride and Magnesium Chloride of high grade purity (> 99%) were purchased from BDH (India) in 2008. The weighing was done by using an electronic balance (model GR-202R, Japan) with a precision of (0.01 mg).

A double stem calibrated [20] pyknometer, Ostwald's viscometer and conductivity meter were purchased from M/S Science Corporation, Allahabad, has been used to determine the density, viscosity and conductance of solvent and solutions. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated using triple distilled water. The viscosity was measured by Ostwald's viscometer. Uncertainty in density and viscosity is nearly 0.01% and 0.02% respectively. The conductance was measured by Centaury digital conductivity meter model CC-60. An electronically operated constant temperature water bath is used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The temperature of the test liquids during the measurements was maintained by circulating water from an electronically controlled thermostatic water bath (JULABO, model ME-3) with an uncertainty of (0.01 K). Fresh solutions of mixture in triple distilled water and methanol have been prepared by variation of concentration keeping total volume constant for measuring parameters at different temperatures.

RESULTS AND DISCUSSION

The values of density (ρ), viscosity (η) and conductance (Λ) for all systems at different temperatures 303.15, 308.15, 313.15, 318.15 and 323.15K are given in Table (1). It is seen that density and viscosity increases with concentration of salt and decreases with increase in temperature whereas conductance increases with increase in temperature as well as concentration of salt. The increasing value of density, viscosity and conductance value shows that there is moderate attraction with solute and solvent molecules and decreased values with temperature shows decrease in intermolecular forces due to increasing thermal energy of system. Q values obtained by Vands equation, classical absorption coefficient $(\alpha/f^2)_{cl}$ and viscous relaxation time (τ) decreases with increase in concentration of salt and increases with increase in temperature given in Table (2) justified presence of strong molecular attraction in the solution. .

Several models (equations) have been put forward from time to time for correlating the viscosity of mixtures with a view to interpret the molecular interaction.

Table 1: Density (ρ), viscosity (η), Conductance(Λ) of systems at different temperature (K)

C (mol.m^{-3}) / T (K)	303.15	308.15	313.15	318.15	323.15
	— $\rho \times 10^{-2}$(kg m^{-3})				
System [i]					
0.050	7.996	7.961	7.948	7.899	7.822
0.100	8.209	8.154	8.143	8.114	8.089
0.150	8.356	8.354	8.326	8.285	8.281
0.200	8.816	8.556	8.509	8.457	8.443
0.250	8.892	8.771	8.718	8.672	8.602
0.300	9.114	9.004	8.924	8.899	8.779
System [ii]					
0.050	8.059	8.013	8.021	7.908	7.874
0.100	8.304	8.214	8.173	8.115	8.104
0.150	8.562	8.404	8.387	8.351	8.315
0.200	8.911	8.602	8.572	8.521	8.424
0.250	9.410	8.930	8.818	8.744	8.711
0.300	9.951	9.887	9.861	9.846	9.834
System [i]	$\eta \times 10^{-2}$ (kgm^{-1}s^{-1})				
0.050	5.881	5.872	5.836	5.404	5.234
0.100	6.862	6.727	6.681	6.509	6.487
0.150	8.132	8.020	7.959	7.555	7.504
0.200	9.346	8.583	8.531	8.180	7.964
0.250	9.427	9.324	9.096	8.374	8.316
0.300	9.498	9.422	9.260	9.096	8.762
System [ii]					
0.050	5.961	5.858	5.842	5.466	5.333
0.100	7.115	7.035	6.931	6.616	6.544
0.150	8.191	8.032	7.984	7.950	7.626
0.200	9.705	9.163	9.123	8.455	8.305
0.250	11.953	11.137	11.015	9.686	9.682
0.300	12.640	12.219	12.119	10.856	10.861
System [i]	$\Lambda \times 10$ (ς^{-1}m^{2}mol^{-1})				
0.050	3.200	3.520	3.800	3.970	4.330
0.100	5.960	6.060	6.460	7.320	7.460
0.150	8.200	8.530	9.140	9.350	9.580
0.200	9.670	9.800	9.900	10.260	10.390
0.250	10.400	9.910	10.740	10.570	10.610
0.300	9.900	11.270	11.510	11.540	11.550
System [ii]					
0.050	1.250	1.470	1.750	1.830	1.690
0.100	2.420	2.640	3.230	3.420	3.150
0.150	3.210	3.600	4.240	4.350	3.900
0.200	3.680	3.910	4.580	4.650	4.120
0.250	3.940	4.150	4.860	4.900	4.340
0.300	4.120	4.260	5.000	5.040	4.450

Table 2: Classical absorption coefficient ((a/f^2)$_{Cl}$, viscous relaxation time (τ) and Vand's coefficient (Q) of systems at different temperature (K)

C (mol.m^{-3}) / T (K)	303.15	308.15	313.15	318.15	323.15
	(a/f^2) Cl				
System [i]					
0.050	9.825	10.245	11.109	11.477	11.748
0.100	10.512	10.916	11.613	11.972	12.202
0.150	11.534	12.581	13.103	13.458	13.556
0.200	11.193	11.296	11.760	11.444	12.428
0.250	10.585	11.559	11.384	10.867	11.353
0.300	10.310	11.042	11.000	11.196	11.206

Table 2: Continued

C (mol.m^{-3}) / T (K)	303.15	308.15	313.15	318.15	323.15
			(a/f^2) Cl		
System [ii]					
0.050	12.011	12.376	12.615	12.240	12.240
0.100	13.061	14.352	14.450	14.428	14.557
0.150	13.466	13.958	14.339	14.919	15.307
0.200	14.365	15.225	15.552	15.538	16.254
0.250	16.143	17.367	17.531	16.167	18.141
0.300	14.222	14.333	15.036	14.978	16.451
System [i]			(τ)		
0.050	6.237	6.419	6.765	6.753	6.808
0.100	6.809	6.951	7.231	7.324	7.417
0.150	7.619	8.037	8.246	8.263	8.286
0.200	7.684	7.591	7.795	7.564	7.925
0.250	7.403	7.858	7.731	7.304	7.523
0.300	7.233	7.582	7.542	7.593	7.537
System [ii]					
0.050	7.144	7.260	7.343	7.073	7.025
0.100	7.934	8.447	8.457	8.339	8.361
0.150	8.400	8.600	8.745	8.979	9.021
0.200	9.157	9.448	9.581	9.354	9.618
0.250	10.419	10.872	10.946	9.964	10.772
0.300	9.575	9.537	9.828	9.454	10.070
System [i]			(Q)		
0.050	5.223	5.201	5.192	5.160	5.110
0.100	5.623	5.585	5.578	5.558	5.540
0.150	5.961	5.960	5.940	5.911	5.908
0.200	6.575	6.381	6.346	6.307	6.297
0.250	6.807	6.714	6.673	6.638	6.585
0.300	7.197	7.110	7.047	7.027	6.932
System [ii]					
0.050	5.175	5.145	5.150	5.078	5.056
0.100	5.593	5.532	5.505	5.466	5.458
0.150	5.960	5.849	5.837	5.812	5.787
0.200	6.868	6.630	6.606	6.567	6.493
0.250	7.174	6.808	6.723	6.667	6.641
0.300	7.525	7.477	7.457	7.446	7.437

Table 3: Values of interaction parameters (T_{12}, H_{12}, d_{12}) of systems at different temperature (K)

C (mol.m^{-3}) / T (K)	303.15	308.15	313.15	318.15	323.15
			(T_{12})		
System [i]					
0.050	1.566	1.553	1.534	1.416	1.361
0.100	1.429	1.392	1.374	1.334	1.319
0.150	1.513	1.482	1.462	1.383	1.363
0.200	1.659	1.514	1.495	1.429	1.381
0.250	1.614	1.586	1.538	1.411	1.390
0.300	1.615	1.592	1.556	1.523	1.455
System [ii]					
0.050	0.872	0.853	0.849	0.792	0.771
0.100	0.832	0.820	0.805	0.766	0.757
0.150	0.859	0.839	0.831	0.826	0.791
0.200	1.125	1.059	1.051	0.971	0.953
0.250	1.236	1.147	1.132	0.992	0.990
0.300	1.200	1.155	1.143	1.021	1.020

Table 3: Continued

C (mol.m^{-3}) / T (K)	303.15	308.15	313.15	318.15	323.15
	---(T_{12})---				
System [i]	---(H_{12})---				
0.050	1.715	1.713	1.703	1.577	1.527
0.100	1.225	1.201	1.193	1.162	1.158
0.150	1.159	1.143	1.134	1.077	1.069
0.200	1.213	1.114	1.107	1.062	1.034
0.250	1.138	1.126	1.098	1.011	1.004
0.300	1.132	1.123	1.104	1.084	1.044
System [ii]					
0.050	1.672	1.643	1.639	1.533	1.496
0.100	1.276	1.262	1.243	1.187	1.174
0.150	1.181	1.158	1.151	1.146	1.100
0.200	1.713	1.617	1.610	1.492	1.466
0.250	1.678	1.563	1.546	1.360	1.359
0.300	1.495	1.445	1.433	1.284	1.284
System [i]	---(d_{12})---				
0.050	7.390	7.496	7.583	7.589	7.683
0.100	8.558	8.641	8.726	8.785	8.911
0.150	9.857	9.945	10.028	10.046	10.167
0.200	11.548	11.515	11.599	11.622	11.710
0.250	12.655	12.744	12.794	12.736	12.856
0.300	14.217	14.310	14.369	14.427	14.483
System [ii]					
0.050	7.250	7.339	7.429	7.449	7.552
0.100	8.598	8.692	8.766	8.800	8.916
0.150	9.855	9.935	10.021	10.108	10.179
0.200	14.398	14.388	14.473	14.410	14.504
0.250	14.838	14.800	14.872	14.700	14.831
0.300	15.089	15.128	15.205	15.070	15.203

Grunberg and Nissan [21] have suggested the logarithmic relation; where (d_{12}) is constant, proportional to interchange energy has negative value throughout decreases with increase in temperature and concentration shows dominance of dispersion forces. According to Tamura & Kurata (T_{12}) is interaction Parameter, depends upon temperature and composition of mixtures have positive values increases with decreases in concentration and increase in temperature showing specific interactions. Hind *et al* have suggested that (H_{12}) is interaction parameter and is attributed to unlike pair interactions have positive values increases with decreases in concentration and increase in temperature shows presence of strong interacrion are given in Table (3). Results of viscosity have been explained by Einstein [22], Vands [23], Moullik [24] and Jones -Dole [25]. These well known equations have been successfully applied to explain the results of viscosity measurements and the viscometric parameters shown by systems in terms of transition state treatment. The values of excess properties for mixtures have been plotted against mole fractions of salts, have been presented in fig. (1-4) respectively. The values of coefficients, *Ai,* were evaluated by using Redlich-kister [26] polynomial equation by the method of least-squares and coefficients A_0, A_1, A_2, A_3 and standard deviation for the mixtures at all temperatures are listed in Table (4-5). The positive values increases with increase in temperature as well as concentration shows presence of strong interactions whereas negative values increases with increase in temperature as well as concentration shows dominance of dispersion forces.
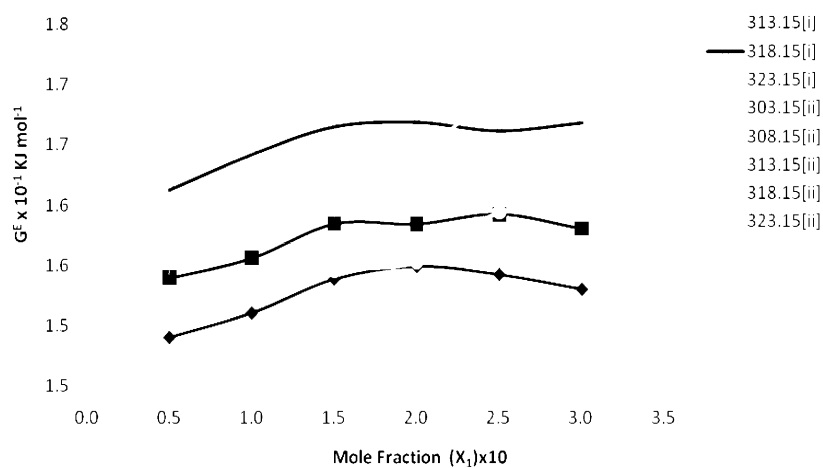
Fig. 1: Variation of Excess Molar Free Energy (G°) with Mole Fraction (X₁) for System [i] and [ii] at 303.15, 308.15, 318.15, 323.15 k
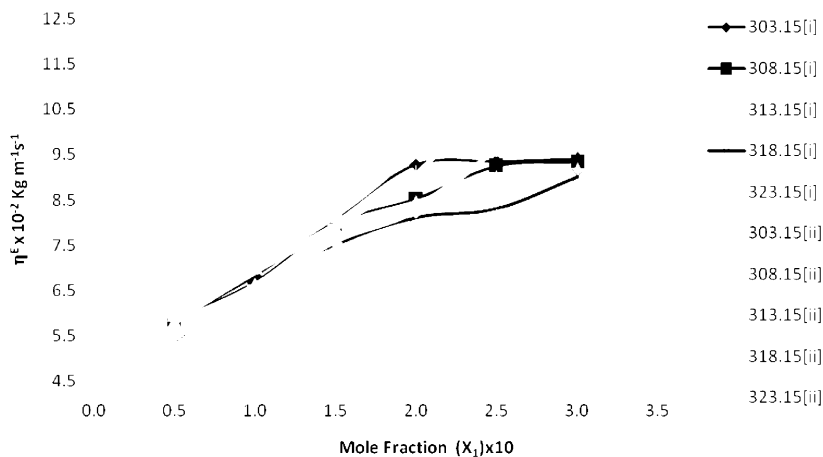

Fig. 2: Variation of Excess Molar Free Energy (η°) with Mole Fraction (X₁) for System [i] and [ii] at 303.15, 308.15, 318.15, 323.15 k
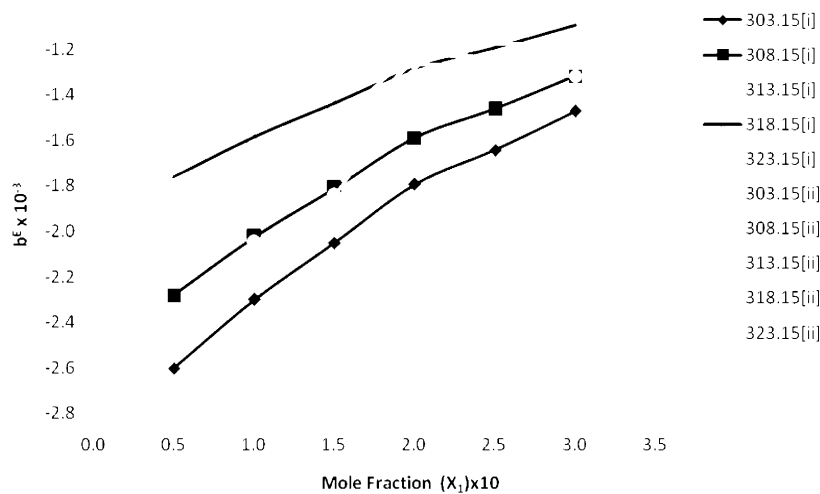

Fig. 3: Variation of Excess Molar Free Energy (b°) with Mole Fraction (X₁) for System [i] and [ii] at 303.15, 308.15, 318.15, 323.15 k
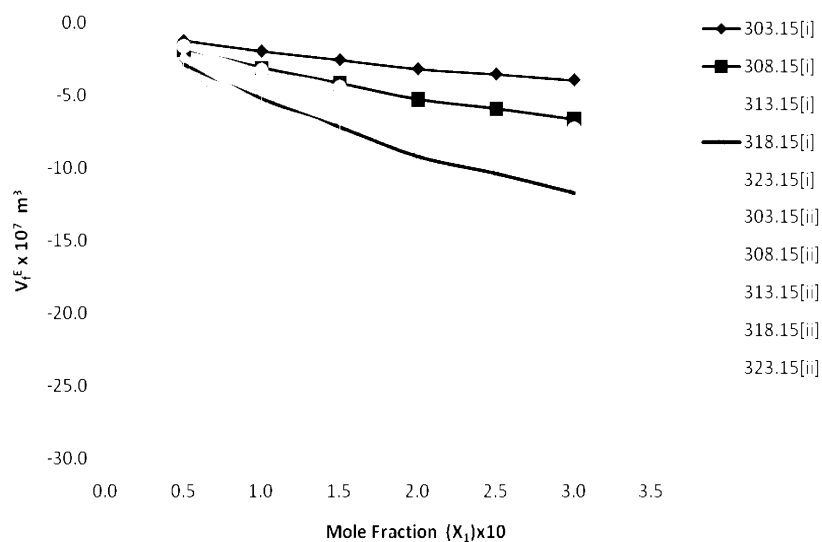
Fig. 4: Variation of Excess Molar Free Energy (V_f^E) with Mole Fraction (X_1) for System [i] and [ii] at 303.15, 308.15, 318.15, 323.15 k

Table 4: Values of excess properties (η^E, G^E, b^E, V_f^E) of systems at different temperature (K)

C (mol.m^{-3}) / T (K)	303.15	308.15	313.15	318.15	323.15
	--(η^E) (kg m^{-1}s^{-1})--				
System [i]					
0.050	5.856	5.847	5.812	5.381	5.212
0.100	6.822	6.688	6.643	6.472	6.452
0.150	8.079	7.968	7.908	7.505	7.456
0.200	9.281	8.519	8.468	8.119	7.905
0.250	9.351	9.250	9.023	8.303	8.248
0.300	9.413	9.338	9.179	9.016	8.685
System [ii]					
0.050	5.929	5.827	5.812	5.439	5.306
0.100	7.064	6.986	6.882	6.573	6.501
0.150	8.122	7.966	7.919	7.892	7.568
0.200	9.627	9.088	9.049	8.389	8.239
0.250	11.857	11.045	10.924	9.604	9.601
0.300	12.526	12.109	12.010	10.759	10.763
System [i]	--(G^E) (kj mol^{-1})--				
0.050	14.900	15.394	15.844	16.122	16.628
0.100	15.103	15.560	16.010	16.418	16.988
0.150	15.384	15.844	16.302	16.649	17.206
0.200	15.487	15.843	16.310	16.687	17.195
0.250	15.422	15.925	16.346	16.614	17.191
0.300	15.300	15.804	16.251	16.682	17.193
System [ii]					
0.050	15.011	15.483	15.940	16.294	16.807
0.100	15.261	15.767	16.212	16.604	17.151
0.150	15.456	15.963	16.427	16.927	17.405
0.200	15.526	15.980	16.452	16.767	17.325
0.250	15.941	16.411	16.897	17.087	17.677
0.300	15.962	16.409	16.876	17.096	17.681
System [i]	--(b^E)--				
0.050	-2.552	-2.231	-1.993	-1.711	-1.556
0.100	-2.250	-1.973	-1.771	-1.533	-1.404
0.150	-2.001	-1.761	-1.588	-1.385	-1.277
0.200	-1.743	-1.540	-1.398	-1.232	-1.146
0.250	-1.593	-1.413	-1.288	-1.144	-1.070
0.300	-1.422	-1.267	-1.163	-1.043	-0.984

Table 4: Continued

C (mol.m^{-3}) / T (K)	303.15	308.15	313.15	318.15	323.15
			-(η^E) (kg m^{-1}s^{-1})-		
System [ii]					
0.050	-2.305	-1.976	-1.724	-1.185	-1.148
0.100	-2.000	-1.748	-1.565	-1.167	-1.168
0.150	-1.787	-1.588	-1.455	-1.155	-1.181
0.200	-1.275	-1.205	-1.189	-1.128	-1.215
0.250	-1.276	-1.205	-1.189	-1.127	-1.215
0.300	-1.268	-1.200	-1.187	-1.129	-1.218
System [i]			-(V_f^E) m^3-		
0.050	-1.233	-1.799	-2.308	-2.871	-3.396
0.100	-1.957	-3.092	-4.105	-5.230	-6.264
0.150	-2.555	-4.160	-5.589	-7.178	-8.634
0.200	-3.176	-5.269	-7.130	-9.200	-11.095
0.250	-3.535	-5.909	-8.019	-10.368	-12.515
0.300	-3.946	-6.644	-9.040	-11.708	-14.145
System [ii]					
0.050	-1.603	-2.519	-3.296	-4.413	-5.195
0.100	-3.278	-5.475	-7.350	-10.052	-11.919
0.150	-4.446	-7.539	-10.179	-13.988	-16.613
0.200	-7.264	-12.515	-17.002	-23.479	-27.930
0.250	-7.257	-12.502	-16.985	-23.455	-27.902
0.300	-7.305	-12.588	-17.103	-23.619	-28.097

Table 5: Redlich- Kister coefficients for third order polynomial and standard deviattion for excess properties for systems at different temperatures

	A$_3$	A$_2$	A$_1$	A$_0$	σ
			---303.15 K---		
System [i]					
G^E (kj mol^{-1})	-4.751.E+01	3.526.E+00	5.485.E+00	1.461.E+01	4.950.E-02
η^E (kg m^{-1}s^{-1})	-34903.65624	11733.07606	1061.074159	503.3739107	23.567731
b^E	0.001521009	-0.008306519	0.007249579	-0.002895109	2.102E-05
V$_f^E$	-2.88268E-07	1.94932E-06	-1.73294E-06	-4.12244E-08	5.122E-09
System [ii]					
G^E (kj mol^{-1})	-2.129.E+01	9.284.E+00	2.896.E+00	1.486.E+01	1.188.E-01
η^E (kg m^{-1}s^{-1})	-4.879.E+04	2.730.E+04	-1.663.E+03	6.230.E+02	3.894.E+01
b^E	-0.142617893	0.058155218	-0.00095498	-0.002379369	0.0001144
V$_f^E$	7.864.E-05	-3.212.E-05	5.524.E-07	-1.204.E-07	6.304.E-08
System [i]			---308.15 K---		
G^E (kj mol^{-1})	-3.673.E+01	3.333.E+00	4.472.E+00	1.516.E+01	6.523.E-02
η^E (kg m^{-1}s^{-1})	-1.982.E+04	6.168.E+03	1.381.E+03	4.999.E+02	1.754.E+01
b^E	1.024.E-03	-6.957.E-03	6.168.E-03	-2.523.E-03	1.827.E-05
V$_f^E$	-5.14692E-07	3.48043E-06	-3.09409E-06	-3.33959E-08	9.145E-09
System [ii]					
G^E (kj mol^{-1})	3.594.E+00	-5.372.E+00	5.265.E+00	1.525.E+01	1.388.E-01
η^E (kg m^{-1}s^{-1})	-1.100.E+04	8.229.E+03	8.241.E+02	5.285.E+02	3.005.E+01
b^E	-1.077.E-01	4.393.E-02	-7.593.E-04	-2.031.E-03	8.536.E-05
V$_f^E$	1.389.E-04	-5.673.E-05	9.755.E-07	-1.814.E-07	1.113.E-07
System [i]			---313.15 K---		
G^E (kj mol^{-1})	-2.617.E+01	-2.839.E+00	5.476.E+00	1.557.E+01	6.267.E-02
η^E (kg m^{-1}s^{-1})	-15297.30938	3608.820699	1737.831972	483.3236513	16.408158
b^E	0.000863459	-0.005983644	0.0053113	-0.00224439	1.576E-05
V$_f^E$	-7.15219E-07	4.83643E-06	-4.29957E-06	-2.71942E-08	1.271E-08
System [ii]					
G^E (kj mol^{-1})	-1.631.E+01	4.671.E+00	3.933.E+00	1.575.E+01	1.417.E-01
η^E (kg m^{-1}s^{-1})	-1.350.E+04	9.541.E+03	5.999.E+02	5.339.E+02	2.525.E+01
b^E	-0.074864751	0.0305438	-0.000533826	-0.001761771	5.89E-05
V$_f^E$	1.904.E-04	-7.778.E-05	1.338.E-06	-2.330.E-07	1.526.E-07
System [i]			---318.15 K---		
G^E (kj mol^{-1})	9.400.E+01	-6.619.E+01	1.531.E+01	1.550.E+01	5.086.E-02
η^E (kg m^{-1}s^{-1})	21452.94099	-15038.83726	4408.765918	347.9796091	17.859571
b^E	0.000603317	-0.004772991	0.004267871	-0.001913262	1.271E-05
V$_f^E$	-9.38813E-07	6.34841E-06	-5.64371E-06	-1.98502E-08	1.668E-08

Table 5: Continued

	A_3	A_2	A_1	A_0	σ
			---303.15 K---		
System [ii]					
G^E (kj mol^{-1})	9.425.E+01	-6.033.E+01	1.429.E+01	1.572.E+01	1.485.E-01
η^E (kg m^{-1}s^{-1})	2.512.E+04	-1.341.E+04	4.136.E+03	3.647.E+02	2.192.E+01
b^E	-0.008708442	0.003557041	-9.08073E-05	-0.001187372	5.68E-06
V_f^E	2.649.E-04	-1.082.E-04	1.861.E-06	-3.069.E-07	2.123.E-07
System [i]			---323.15 K---		
G^E (kj mol^{-1})	1.068.E+02	-7.518.E+01	1.711.E+01	1.594.E+01	2.773.E-02
η^E (kg m^{-1}s^{-1})	22113.64382	-16368.28976	4743.626369	319.7815275	8.293719
b^E	0.000428347	-0.004026033	0.00364621	-0.001729249	1.089E-05
V_f^E	-1.14204E-06	7.72267E-06	-6.86542E-06	-1.44335E-08	2.029E-08
System [ii]					
G^E (kj mol^{-1})	7.491.E+01	-4.867.E+01	1.256.E+01	1.630.E+01	1.343.E-01
η^E (kg m^{-1}s^{-1})	2.150.E+04	-1.056.E+04	3.578.E+03	3.764.E+02	1.701.E+01
b^E	0.008436669	-0.003436201	2.01732E-05	-0.001141536	8.139E-06
V_f^E	3.159.E-04	-1.290.E-04	2.219.E-06	-3.593.E-07	2.532.E-07

Table 6: Values of Eη, A, ΔH and ΔS for system at different concentrations

Conc.	Eη		ΔH	ΔS	EΛ	Λ_0
mol.m^{-3}	KJ mol^{-1}	A	KJ mol^{-1}	KJ mole^{-1}K^{-1}	KJ mol^{-1}	(V^{-1}m^2 mol^{-1})
1 [i]	5.112	79.024	4.337	-0.461	-11.814	35.122
2 [i]	2.370	267.442	1.806	-0.452	-10.362	35.562
3 [i]	3.582	197.572	3.170	-0.456	-6.576	11.204
4 [i]	6.012	84.361	4.391	-0.460	-3.077	3.264
5 [i]	5.815	95.150	4.581	-0.460	-1.697	2.005
6 [i]	3.181	271.006	1.803	-0.452	-5.475	9.134
1 [ii]	4.733	92.189	3.806	-0.459	-13.539	28.826
2 [ii]	3.719	163.840	2.748	-0.455	-12.917	42.254
3 [ii]	2.482	306.407	1.454	-0.450	-9.568	15.180
4 [ii]	6.381	76.869	4.407	-0.460	-6.627	5.328
5 [ii]	9.134	31.823	6.298	-0.464	-5.978	4.402
6 [ii]	6.854	84.042	6.427	-0.465	-5.364	3.584

Table 7: Values of $\eta_{0\eta}\Lambda_0$Eη, $\Delta\mu_1^0$, $\Delta\mu_2^0$ and B for system at different temperatures (K)

	$\eta_0\Lambda_0$ (ς^{-1}m mol^{-1}kgs^{-1}) x 10^{-4}				
	303.15	308.15	313.15	318.15	323.15
1 [i]	2.011	2.039	0.637	0.177	0.107
2 [i]	2.500	2.413	0.754	0.201	0.123
3 [i]	2.642	2.576	0.791	0.227	0.136
4 [i]	3.174	3.147	0.984	0.242	0.146
5 [i]	3.219	3.163	0.993	0.256	0.151
6 [i]	3.376	3.354	1.047	0.285	0.161
1 [ii]	1.651	2.422	0.864	0.289	0.234
2 [ii]	2.052	2.867	1.021	0.329	0.270
3 [ii]	2.168	3.060	1.072	0.370	0.299
4 [ii]	2.605	3.739	1.333	0.394	0.320
5 [ii]	2.642	3.759	1.345	0.418	0.332
6 [ii]	2.771	3.986	1.418	0.465	0.354
B[i]	-0.133	-0.217	-0.335	0.237	0.603
B[ii]	1.548	1.347	1.291	1.240	1.846
$\Delta\mu_1^0$ (KJ mol^{-1})[i]	77.73	81.25	79.23	80.41	84.02
$\Delta\mu_2^0$ (KJ mol^{-1})[i]	77.40	80.69	78.35	81.04	85.64
$\Delta\mu_1^0$ (KJ mol^{-1})[ii]	77.47	84.32	81.04	89.94	89.86
$\Delta\mu_2^0$ (KJ mol^{-1})[ii]	81.36	87.76	84.40	93.22	94.82

Table 8: Redlich- Kister coefficients for third order polynomial and standard deviation for walden product ($d/dT(h_0L_0)$) and Jone's- dole coefficient (B) for systems at different concentrations

	A_3	A_2	A_1	A_0	σ
	$d/dT(\eta_0\Lambda_0)$ (walden product)				
1 [i]	0.001212823	-1.136713459	354.9088597	-36913.27829	0.2467655
2 [i]	0.001364165	-1.277740112	398.6725271	-41435.69049	0.2798804
3 [i]	0.001461906	-1.369382898	427.2979532	-44414.38571	0.3115242
4 [i]	0.001854869	-1.73805372	542.525736	-56412.06767	0.3661896
5 [i]	0.001831094	-1.715581965	535.4464776	-55668.74158	0.3676608
6 [i]	0.001949874	-1.827098972	570.3267642	-59303.26664	0.4005463
1 [ii]	0.001900394	-1.786383031	559.4756882	-58378.8017	0.319247
2 [ii]	2.196.E-03	-2.064.E+00	646.299	-67420.2	0.3662
3 [ii]	2.341.E-03	-2.200.E+00	688.909	-71866.0	0.4077
4 [ii]	2.936.E-03	-2.760.E+00	864.224	-90169.0	0.474
5 [ii]	2.914.E-03	-2.739.E+00	857.676	-89483.2	0.478
6 [ii]	0.003083234	-2.89812005	907.610076	-94699.27391	0.5212944
B (Jones- Dole)	A_4	A_3	A_2	A_1	A_0
[I]	-0.000108183	0.135330843	-63.46788854	13225.63965	-1033236.5
[ii]	5.27353E-05	-0.065683193	30.6767634	-6367.285288	495569.34
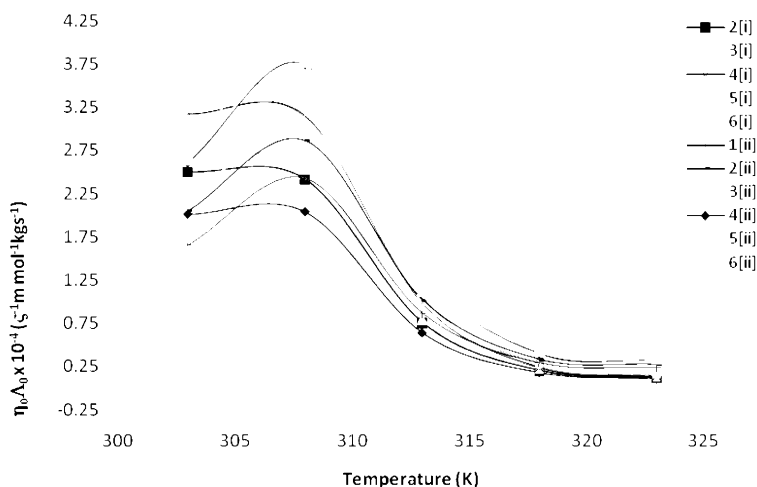
Fig. 5: Variation of Excess Molar Free Energy $\eta_0\Lambda_0$ with Mole Fraction (X_1) for System [i] and [ii]

With the help of viscosity data various thermodynamic parameters ΔH, ΔG and ΔS and Jones-Dole constant A & B have been calculated for mixtures at different temperatures and given in Table (7). A is Falkenhagen coefficient, a measure of solute-solute interactions [27] and B is Jones-Dole coefficient an empirical constant and is indicative of solute-solvent interactions. B-coefficient [28] is positive suggesting the presence of strong solute-solvent interactions as compared to solute-solute interactions.

The free energy of activation ?G is almost constant for mixtures indicating charge transfer complexes in other systems [29]. The effect of temperature on the viscosity and conductance is given by Arrhenius equation were calculated from the slope of linear plot of log E_η and log E_Λ vs. 1/T and values of slope and intercept are given in

Table (7) where A and Λ^0 is constant and $E\eta$ and E_Λ is activation energy for viscous flow[30]. The energy of activation should be less than energy of activation E_Λ for viscous flow. The viscosity data has also been analyzed on the basis of transition state theory of relative viscosity of electrolytic solutions as suggested by Feakins *et al* [31]. The values of $\Delta\mu_1^0$ (free energy of activation per mole of solvent) and $\Delta\mu_2^0$ free energy of activation per mole of solute) were calculated and is given in Table (8) suggested for increase in interaction of solute ions by the solvent molecules as a result of weakening of forces among molecules at transition state. The conductance increases with increase in ionic mobility of free ions at dilution. It has been emphasized by a number of workers that positive value of Walden product $\eta^0\Lambda^0$ and Jones-Dole coefficient B given in Table (8 & 9) and in fig.(5 - 6)
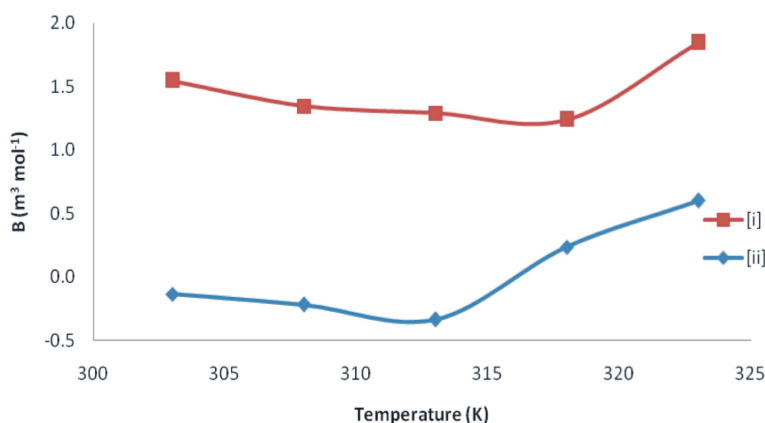
Fig. 6: Variation of Excess Molar Free Energy B with Mole Fraction (X_1) for System [i] and [ii]

indicates the structure making capability of salt in water and is more important criteria for determining solute-solvent interactions.

Possible types of solute-solvent interaction exists in between curcumin and methanol, ion-ion interaction in between ions (Na^+, Mg^{++}) and water, ion-polar site interaction in between ions and polar sites of curcumin (phenolic hydroxyls and diketo groups), ion-non polar interaction in between ions with CH_3OH, non polar-polar interaction or hydrophobic- hydrophilic interaction exists in between curcumin, water and metal ions with pi e- cloud of two benzene rings (aromatic nucleus) produces significant change in the physical properties of curcumin.

Theory and Calculations:

Jones- dole eqn.	$\eta / \eta_0 = 1 + Ac^{0.5} + BC$	(1)
Einstein eqn	$\eta / \eta_0 = 2.5\ V_m\ C$	(2)
Vand's eqn.	$1/c = (0.921/(V_m))^{-1}$	
	$(1/\log \eta / \eta_0) + QV_m$	(3)
Moulik Eqn.	$(\eta / \eta_0)^2 = M + K\ C^2$	(4)
Energy of Viscous flow	$E\eta = Ae^{(E_\eta / RT)}$	(5)
Energy of conductance	$E_\Lambda = \Lambda^0 e^{(E_\Lambda / RT)}$	(6)
For solvent	$\Delta\mu_1^0 = RT \ln \eta_{0V1}^0/hN$	(7)
For Solute	$\Delta\mu_2^0 = \Delta\mu_1^0 + (RT/\bar{V}^0)$	
	$(1000\ B - (\bar{V}_1^0 - \bar{V}_2^0)$	(8)
Free energy	$\Delta G^* = RT \ln (\eta\ V_m / h\ N)$	(9)
	$\Delta G^* = \Delta H^* - T\ \Delta S^*$	(10)
Grunberg and Nissan Parameter	$\ln\eta = X_1\ln\eta_1 + X_2 \ln\eta_2 + X_1X_2d_{12}$	(11)
Tamura and Kurata eqn	$\eta = X_1V_{m1}\eta_1 + X_2V_{m2}\eta_2$ $+ 2(X_1X_2V_{m1}V_{m2})^{0.5}\ T_{12}$	(12)
Hind *et al*	$\eta = X_1^2\eta_1 + X_2^2\eta_2 + 2X_1X_2\ H_{12}$	(13)

Excess Gib's free energy of activation	$G^E /RT = \ln (V/\eta_2V_2)$ $-X_1\ln(\eta_1\ V_1 /\eta_2V_2)$	(14)
Excess viscosity	$\eta^E = \eta - (X_1\eta_1 + X_2\eta_2)$	(15)
Classical absorptiom coefficient	$(\alpha/f^2)_{Cl} = 8\pi^2\eta/(3u^3\rho)$	(16)
Viscous relaxaxation time	$\tau = 4\eta / 3\rho u^2$	(17)
Redlich kister Eqn.	$Y^E = X_1(1-X_1)\ \Sigma a_i\ (2X_1-1)^i$	(18)

Where, ΔG^*, ΔH^*, ΔS^* are standard change in free energy, enthalpy and entropy respectively, K is a temperature dependent function equal to 4.25×10^9 for all liquids, R is gas constant, T is absolute temperature and b is cubic packing factor assumed to be 2 for all liquids and sol

CONCLUSION

Densities and viscosities of curcumin in aqueous metal electrolyte solutions containing NaCl and $MgCl_2$ have been determined experimentally at 303.15, 308.15, 313.15, 318.15 and 323.15K. The properties [32-33] of these systems are discussed in terms of charge, size and hydrogen bonding effect. The structure making and breaking capabilities of these smaller ions are weak as discussed by their B- coefficient values. The studies of viscous behavior of molecules in solutions and thermodynamic parameters [34] is important in understanding the mechanism of transport process provide valuable information regarding the size and shape of these molecules. It can be concluded that being a strong electrolyte sodium chloride has higher conductance than magnesium chloride suggests [35]

the existence of ion-solvent interaction hydrophilic-hydrophobic interactions over ionic- hydrophilic interactions. From the co-sphere overlap model it can be concluded that ion-solvent interactions are dominating over the solute-co-solute interactions. Viscosity is another important parameter in understanding the structure as well as molecular interactions occurring in the solutions. B-coefficient [36] is known as measure of order and disorder introduced by the solute into the solvent and a measure of ion-solvent interaction and relative size of the solute and solvent molecules.

Study of antioxidants is a burning field of science nowadays as is related to ageing process and several other diseases such as cancer, diabetes, neurodegenerative diseases, allergy and ophthalmologic problems. Curcumin is chosen for the molecular interaction studies because it has great potential as drug. Bio chemists now firmly believe that the characteristic of living organism such as selective permeability across cell- membranes, muscle contractions, hearing and memory processes and nerve conduction etc. can be interpreted in terms of co-coordinative interactions of small and large molecules. Therefore we have calculated different physico-chemical data to study the molecular interaction between curcumin and metal ions. Metal ions play several different roles in biological processes. Such types of studies will be useful in understanding the mechanism of action of antioxidants in the living systems. The interactions of ions and antioxidant provide important information about physiological system and can be used to understand the mechanism of their metabolism in living system. Na^+ ions play major role in nervous system and Mg^{++} ion in muscular system and respiratory system. The excellent predictive capability over the entire range of data indicates that cations with higher charge densities ($Mg^{2+} > Na^+$) are more heavily solvated and thus cause a greater increase in viscosity as the solute concentration is increased. Therefore these two ions are selected to study the interaction with curcumin as an antioxidant.

ACKNOWLEDGMENT

REFERENCES

1. Jayaprakasha, G.K., J.M. Rao and K.K. Sakariah, 2002. Improved HPLC method for the determination of curcumin, demethoxycurcumin and bisdemethoxycurcumin. J. Agri. and Food Chem., PMID: 12059141. 50(13): 3668-72.

2. Priyadarsini, K.I., D.K.Maity, G.H. Naik, M.S. Kumar, M.K. Unnikrishnan, J.G. Satav and H. Mohan, 2003. Role of phenolic O-H and methylene hydrogen on the free radical reactions and antioxidant activity of curcumin, Free Radical Biology and Med., DOI: 10.1016/S0891-5849(03)00325-3. 35(5): 475-484.

3. Khopde, M.S., K.I. Priyadarsini, P. Venkatesan and M.N.A. Rao, 1999. Free radical scavenging ability and antioxidant efficiency of curcumin and its substituted analogue. Biophysi. Chem. DOI: 10.1016/S0301-4622(99)00070-8. 80(2): 83-89.

4. Aggarwal, B.B., A. Kumar and A.C. Bharti, 2003. Anticancer potential of curcumin: preclinical and clinical studies. Anticancer Res., www. ncbi. nlm. nih. gov/ pubmed/12680238. 23(1A): 363-98.

5. Arun, N. and N. Nalini, 2002. Efficacy of turmeric on blood sugar and polyol pathway in diabetic albino rats. Plant foods hum nutrition. 57(1): 41-52. www. curcuminoids. com/ research00.htm.

6. Fusheng, Y., P. Giselle, A.N. Lim, O.J.U. Begum and R.S. Mychica, 2005. Curcumin Inhibits Formation of Amyloid â Oligomers and Fibrils, Binds Plaques and Reduces Amyloid in Vivo. J. Bio. Chem., 280: 5892-590. DOI: 10.1074/jbc.M404751200.

7. Koide, T., M. Nose, Y. Ogihara, Y. Yabu and N. Ohta, 2002. Leishmanicidal effects of Curcumin in vitro Biology. Pharmacology Bulletin, 25(1): 131-3. www. ayurvedicmedicine4u.com/ references.

8. Heng, M.C., M.K. Song, J. Harker and M.K. Heng, 2000. Drug-induced suppression of phosphorylase kinase activity correlates with resolution of psoriasis as assessed by clinical, histological and immune histochemical parameters. Br. J. Dermatol., 143(5): 937-49. PMID: 11069500

9. Elena, T.P., J.C. Gooz, A. Oates, L.B. Richard and M.S. Stanley, 2004. Curcumin-Induced Apoptosis in Scleroderma Lung Fibroblasts, Role of Protein Kinase. American J. Respiratory Cell and Molecular. Biol., 31: 28-35. DOI: 10.1165/rcmb.2003-0354O

10. Banipal, T.S., J. Kaur, P.K. Banipa and K. Singh, 2008. Study of Interactions between Amino Acids and Zinc Chloride in Aqueous Solutions through Volumetric Measurements at T = (288.15 to 318.15) K, J. Chem. Eng. Data., 53(8): 1803-1816. DOI: 10.1021/je8001464.

11. Santosh, M.S., D.K. Bhat and A.S. Bhat, 2009. Molecular Interactions in Glycylglycine-MnCl$_2$ Aqueous Solutions at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K, J. Chem. Eng. Data., 54 (10): 2813-2818. DOI: 10.1021/je800732f.

12. Mishra, P.P., N.C. Das and P.B. Das, 1979. Ion-solvent interaction from viscosity, apparent molar volume and conductivity data of bromates, iodates and sulphates of potassium and sodium in dioxane-water mixtures at different temperatures. Cellular and Molecular Life Sci., 35(6): 724-725. DOI 10. 1007/BF01968204.

13. Pan, H.P., T.C. Bai, Wang and D. Xu, 2009. Density, Viscosity and Electric Conductance of a Ternary Solution of (Nicotinic Acid + Polyethanol + Water). J. Chem. Eng. Data. Article ASAP, DOI: 10.1021/je900781y, Publication Date (Web): November 18,

14. Banipal, T.S., D. Kaur, P.K. Banipal and G. Singh, 2007. Thermodynamic and transport properties of l-serine and l-threonine in aqueous sodium acetate and magnesium acetate solutions at T = 298.15 K. J. Chem. Thermo., 39(3): 371-384. DOI: 10. 1016/ j.jct. 2006. 08.003.

15. Yang, J.Z. and X.H. Chang, 2006. Thermodynamics of Ion Pair of Magnesium Sulfate in Mixed Solvent. Chem. Res. in Chine. Univ., 22(3): 403-405. DOI: 10. 1016/S1005-9040(06)60128-116.

16. Parmar, M.L. and S.C. Attri, 2007. A comparative study of partial molar volumes of some common, tetra-alkyl ammonium and multivalent electrolytes in aqueous and binary aqueous solutions of urea. J. Mol. Liquids. 136(1-2): 38-43 DOI: 10. 1016/j. molliq. 2007. 01.004.

17. Nikam, P.S.P., S. Ravindra, A.B. Sawant and M. Hasan, 2005. Limiting Ionic Partial Molar Volumes and Viscosities of Cs$^+$, Na$^+$, (C$_4$H$_9$)$_4$N$^+$, Cl$^-$, Br$^-$, I$^-$ and BPh$_4^-$ in Aqueous Acetone at 308.15 K. J. Chem. Eng. Data., 50(2): 487-491. DOI: 10.1021/je049698c

18. Ravindranath, V. and N. Chandrashekhera, 1981. Pharmacology of diferuloyl methane (curcumin), a non-steroidal anti-inflammatory agent. J Pharm. Pharmacol. Toxicol., 20: 251-257. DOI: 10.1016/0300-483X (81)900561.

19. Wang, Y.J., M.H. Pan, A.L. Cheng, L. Lin, Y.S. Ho and J.K. Lin, 1997. Stability of curcumin in buffer solutions and characterization of its degradation products. J. Pharma. Biomedi Analysis. 15(12): 1867-72. DOI: 10.1016/S0731-7085(96)02024-9

20. Srivastava, R., A.R. Saksena and A. Gupta, 2010. Viscometric Studies on the Molecular Association of Biomolecules Based on Thermodynamic Parameters Supported by UV Spectra, Asian J. Appl. Sci., 3(1): 13-24. DOI: 10.3923/ajaps.2010.13.24.

21. Grunberg, L. and A.H. Nissan, 1949. Densities and viscosities of 2-methoxy-2-methylpropane + 2-methyl, Nature. 164:799. DOI/abs/10.1021/je00011a019

22. Einstein A. Annalen Der Physik, 1911. 34591 Einstein's Annalen Papers: The Complete Collection 1901 - 1922 by Jurgen Renn (Editor), Bestimmung der s e a r c h . b a r n e s a n d n o b l e . c o m / E i n s t e i n s - Annalen.../9783527405640 Moleküldimensionen

23. Vand, 1948. Transport characteristics of suspension: VIII. J. Physical Colloid Chemistry. 52: 277, linkinghub. elsevier.com/ retrieve/ pii/ 0095852265900164

24. Moullik, S.P., 1972. Electrolyte conductance in solutions of non-electrolytes-urea, sucrose, glycerol and mannitol. Electrochimica Acta, 17(8): 1491-1497. DOI:10.1016/0013-4686 (72) 80090-2

25. Jones, G. and M. Dole, 1929. Viscosities of Aqueous Solutions of Strong Electrolytes with Special Reference to Barium Chloride. J. Ameri. Chem. Soc., 51: 2950. linkinghub. elsevier. com/ retrieve/ pii/0013468667800628.

26. Redlich, O. and A.T. Kister, 1948. Algebric representation of thermodynamic properties and classification of solutions. Ind. Eng. Chem., 40: 345-348. linkinghub.elsevier. com/retrieve/ pii/ S002 1961499906158

27. Gupta, R. and M. Singh, 2005. Viscometric and thermodynamic studies of interactions in ternary solutions containing sucrose and aqueous alkali metal halides at 293.15, 303.15 and 313-15 K, J. Chem. Sci., 117(3): 275-282. cat.inist.fr/?aModele=afficheN andcpsidt=16981710

28. Pradhan, P., R.S. Sah and M.N. Roy, 2009. Ion-solvent and ion-ion interactions of sodium molybdate and sodium tungstate in mixtures of ethane-1, 2-diol and water at 298.15, 308.15 and 318.15 K.J. Mol. Liq., 144(3): 149-154. DOI:10.1016/j.molliq.2008.11.001.

29. Takeda, Y., T. Watanabe, H. Yamada and S. Katsuta, 2003. Thermodynamic study on transfer between polar solvents of 15-crown-5, benzo-15-crown-5 and their 1:1 complexes with alkali metal ions. J. Mol. Liq., 108(1-3): 151-173. DOI:10.1016/S0167-7322(03)00180-6

30. Glasstone, S., K.T. Laidler and H. Eyring, 1941. "The Theory of rate processes" Mc Graw Hill, New York, pp: 480.

31. Feakins, D., D.J. Freemantle and K.G. Lawrance, 1974. Transition State Treatment of the Relative Viscosity ofElectrolyteSolutions.Application to Aqueous, Nonaqueous and Methanol+Water Systems. J. Chem. Soc. Faraday Trans., 70: 795-806. linkinghub. elsevier. com/ retrieve/pii / S0167732201002434

32. Dash, U.N., M.R. Patnaik and C.R. Bhattacharjee, 1998. Density, viscosity and ultrasonic study of tris (acetyl acetonato) cobalt(III) in alcohols. J. Mol. Liq., 75(3): 253-260. DOI:10.1016/S0167-7322(97)00105-0.

33. Badarayani, R., B. Dilip and A. Kumar, 2005. Effect of NaBr, KCl, KBr and $MgCl_2$ on Viscosities of Aqueous Glycine and l-Alanine Solutions at 298.15 K. J. Chem. Eng. Data., 50(3): 1083-1086. DOI: 10.1021/je050048y

34. Pan, H.P., T.C. Bai and X.D. Wang, 2009. Density, Viscosity and Electric Conductance of a Ternary Solution of (Nicotinic Acid + Polyethanol + Water), J. Chem. Eng. Data., Article ASAP DOI: 10. 1021/je900781y, Publication Date (Web): November 18.

35. Rodríguez, H. and J.F. Brennecke, 2006. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid, J. Chem. Eng. Data., 51(6): 2145-2155. DOI: 10. 1021/ je0602824.

36. Yan, Z., H. Wang, W. Liu and J. Lu, 1999. Apparent molar volumes and viscosity B-coefficients of some α-amino acids in aqueous solutions from 278.15 to 308.15 K. Thermochimica. Acta., 334(1-2): 17-27. DOI: 10. 1016/S0040-6031(99)00107-0