13602



Available online at www.elixirpublishers.com (Elixir International Journal)

Chemical Physics

Elixir Chem. Phys. 56A (2013) 13602-13606



Ultrasonic and EPR Studies In Water-Glycerine Mixtures With Mnso₄ & Voso₄

G.Rajarajan

Department of Physics, Mahendra Engineering College, Namakkal -637 503.

ARTICLE INFO

Article history: Received: 25 July 2012; Received in revised form: 15 March 2013; Accepted: 20 March 2013;

Keywords

Observed absorption, Electron paramagnetic resonance, MnSO₄, VOSO₄

Introduction

Earlier ultrasonic velocity study on glycerine - water mixtures with paramagnetic ions [1] has thrown light on the nature of association, dissociation and also on the complex formation between glycerine-water mixtures and the paramagnetic ions. The ultrasonic velocity and absorption studies on various mixtures with paramagnetic ions have proved that the molecular interaction can be well understood [2-9]. Electron paramagnetic resonance (EPR) technique can be extensively used to study about the structural phase transitions in the crystal, since it is sensitive to local symmetry and is also used in the study of ionic association in water mixtures. The magnetic properties of transition metal ions in various solids or lattices are directly linked with the electronic structure of the embedded ions.

Hence with a view to study the molecular interaction in the complex formation and variation of line width with concentration, the present study is undertaken in water – glycerine mixtures with $MnSO_4 & VOSO_4$, since these transition metal elements in their common oxidation state are known to form complexes in mixtures. Further, these metal ions are EPR active even at room temperature.

Experimental:

All the chemicals used in the present study are of AR/BDH quality and are used as such without further purification. Waterglycerine mixtures of respective volume proportions, solution A (9:0.9), solution B (8:1.9) and solution C (7:2.7) are prepared. Solutions of MnSO₄ and VOSO₄ in 0.1-0.6 (w/w) concentration range are prepared separately by dissolving known amounts of the salt in double distilled water. From the above solution, 0.1ml is added to the said water-glycerine mixtures. The ultrasonic velocity and absorption has been measured at a frequency of 7 MHz using a pulsed power oscillator. The density and viscosity of the solutions are measured using a specific gravity bottle and Ostwald's viscometer respectively. The temperatures of the solutions are maintained at 303 K with an accuracy of ± 0.02 K in an electronically controlled thermostatic water bath.

ABSTRACT

Ultrasonic velocity, absorption and EPR measurements are carried out with manganous sulphate (MnSO₄) & vanadyl sulphate (VOSO₄) salts in water-glycerine mixtures in the concentration range 0.1-0.6 (w/w). The results are discussed on the basis of Hall's two state model and molecular interaction due to complex formation between water-glycerine and water-paramagnetic ions. The spin Hamiltonian parameters for MnSO₄ & VOSO₄ from EPR spectra have been evaluated.

© 2013 Elixir All rights reserved.

The solution spectra of manganous sulphate and vanadyl sulphate in 0.1-0.6(w/w) concentration range are recorded at room temperature in JEOL JES TE100 ESR spectrometer having 100kHz modulation and operating at X-band frequency. DPPH with g value of 2.0036 is used as an internal field marker.

Results and Discussion:

The measured and computed parameters viz., density, shear velocity, adiabatic compressibility, viscosity, ultrasonic observed absorption, classical absorption, excess absorption and relaxation time of water - glycerine mixtures with paramagnetic ions are given in tables 1 & 2. The hyperfine (A) and g values, calculated from EPR spectra for water - glycerine mixtures with paramagnetic ions, are given in tables 3 & 4. The variation of ultrasonic velocity and observed absorption with concentration for water - glycerine with MnSO₄ and VOSO₄ are given in figures 1 and 2. The EPR spectra are recorded for all the concentrations. A representative EPR spectra of water-glycerine mixtures with MnSO₄ & VOSO₄ at 0.4 concentration are given in figures 3 and 4. In all the systems studied, as the glycerine volume increases, there is an increase in the value of the measured and computed parameters. It is more in solutions A and B and is less in solution C. The values of density and viscosity of these systems increases with increase in the paramagnetic ion concentration.

Ultrasonic velocity and absorption studies:

The ultrasonic velocity is greater in solution C than in solution A and solution B, in the absence of paramagnetic ions, indicates that the association between water and glycerine molecules in strongest in solution C. This association is due to the formation of hydrogen bonds [10-11]. It may be inferred also that hydrogen bonding in solutions A and B is weak compared to that of solution C. The adiabatic compressibility is least in solution C indicating that the medium is less compressible; hence velocity is higher in solution C. It is seen from the figure that the ultrasonic velocity increases with the increase of paramagnetic ion concentration for all the systems. When the paramagnetic ion is added, a small increase, obtained in the three solutions A, B & C, may be due to the breaking of

already formed water-glycerine association by SO_4^{2-} ions. It is confirmed by the decrease of adiabatic compressibility for all the systems.

The variation of observed absorption (figure 2) in all the solutions indicates that as the glycerine volume increases, the observed absorption also increases. The addition of paramagnetic ions viz., $MnSO_4$ and $VOSO_4$, the observed absorption shows a increase in the initial concentration and decrease in 0.3 concentration for $MnSO_4$ & in 0.4 concentration for $VOSO_4$ and this shows that the system is stabilized very much through association.

The addition of paramagnetic ions increases the value of observed absorption (figure 2) in solutions A, B & C, due to the breaking of water – glycerine association by $SO_4^{2^-}$ ions. Hence two possible complexes are in this process: (a) ion – water complex and (b) ion – water – glycerine complex. The earlier ultrasonic velocity studies clearly show that the possibility of paramagnetic ion – glycerine complex is remote [1]. In the present study also, the paramagnetic salt – glycerine complex is unlikely. The formation of the complexes due to interaction strengthens the association in a system and hence an increase in absorption is observed.

In the present system also the interaction between water and paramagnetic ion is due to a possible two types of complexes and hence the small increase observed may be due to competition between the two complexes. The net resultant shows a small increase in the absorption, because the two complexes strengthen the medium.

The mechanism of complex formation can be explained by resorting to Hall's two state model in which the two possible states are,

(a) paramagnetic ion + glycerine +water and

(b) free water monomers.

 $MnSO_4$, when dissolved in water, is broken into Mn^{2+} , $[Mn(H_2O)_6]^{2+}$ and SO_4^{2-} ions. When the glycerine is added to the above mixture, glycerine replaces the water molecule, whose coordination number gets changed as, $\{[Mn(H_2O)_5]^{2+} + glycerine\}$ and as the glycerine volume increases changes become pronounced. This kind of behavior results in the change of line width of EPR spectrum (figures 3&4). The line width change indicates the relaxation of the medium in the presence of paramagnetic ions. Such a change in the absorption is observed in all the concentrations studied. The observed absorption for all the solutions is several times greater than the classical absorption, which is the characteristic feature of the mixtures having associated naturally through hydrogen bonding [12].

The classical absorption calculated on the basis of the shear viscosity and velocity, changes appreciably in the composition studies. The change in classical absorption may be due to viscosity changes. The observed absorption is more than classical absorption which is due to complex formation in associated systems [13-15]. Such a variation is observed in the present study thereby confirming the complex formation.

It can be inferred from the absorption studies, where there is definite molecular interaction through hydrogen bonding, the ultrasonic absorption shows a large increase and other associated parameters also show change. However in the case of systems, where the interaction is not specific and the addition of the structure breaking compounds, results in non-specific association leading to two types of complexes. The increase in absorption is less pronounced and such a change is observed in the present study. The relaxation time shows a similar variation as of observed absorption.

Electron paramagnetic resonance (EPR) studies:

The recorded EPR spectra for $MnSO_4$ and $VOSO_4$ are shown in figures 3 & 4 and the obtained spin Hamiltonian values are given respectively in tables 3 & 4. Due to the presence of half filled d-orbital, the resultant orbital angular momentum of Mn(II) is zero. Mn(II) gives well resolved EPR spectra even at room temperature [16-19]. EPR of Mn(II), high spin d⁵ ion, has been studied quite extensively in the investigation of structural and dynamic aspects of crystalline state, phase transitions etc [20-25]. EPR for the vanadium has been studied under various oxidation states [26-28]. The vanadyl ions are used extensively as an impurity probe for EPR studies due to its most stable nature.

The g and A values have been calculated using the standard equation,

$$\mathbf{g} = \left(\frac{\mathbf{h}}{\beta}\right) \left(\frac{\mathbf{v}}{\mathbf{B}}\right)$$

Here h is Planck's constant, β is Bohr magneton, ν is frequency and B the resonance field. For example, in the case of Mn(II), a sextet is obtained. The center of the sextet is B and the g value is calculated.

Similarly, the hyperfine-coupling constant for a system having n number of lines is,

$$\mathsf{A} = \frac{(\mathsf{B}_{\mathsf{n}} - \mathsf{B}_{\mathsf{1}})}{(\mathsf{n} - \mathsf{1})}$$

where B_1 is the resonance field of the first line and B_n is the resonance field of the n^{th} line.

With these two equations, g and A have been calculated and given in tables 3&4 respectively for Mn(II) and vanadyl systems. As expected, the g values for all the systems in close to 2.006 and hyperfine value to 9.2 to 9.3 mT. However, an intensity change has been noticed. Similar closeness in g and A values is noticed for al the vanadyl systems studied in the present work. The intensity of peak height as the glycerine volume increases for all the systems studied. As the paramagnetic ion concentration increases, there is a non-linear variation in the peak height. Peak height is defined as the intensity of the first hyperfine line, assuming equal line widths. This non-linear variation is attributed to the complex formation between water – glycerine – paramagnetic ions.

Conclusions:

The spin Hamiltonian parameters evaluated are found to be comparable with that of reported systems. It has been found that the relaxation time gets modified in the presence of high viscous liquids in aqueous paramagnetic ion solutions.

The present study also reveals that the ultrasonic velocity and absorption studies is better opted to get a clear cut picture about molecular association and EPR studies seems to give a overall picture of the complex formation in which the paramagnetic ions has been incorporated. Further work is needed to get an idea of relaxation values from EPR measurements.

References:

1.T. K. Nambinarayanan and A. Srinivasa Rao, Acustica, 53 (1983) 264

2.A. Sree Devi, M. Phil., Thesis, University of Madras, 1985

- 3.R. Suharamann and F. Breyer, Z. Phys. Chem. B20 (1933) 17
- 4.M. Eigen and E. Wicke, Z. Elektro. Chem. 55 (1951) 344.

Ultraso	nic	velocity	and abs	orption	values fo	or water - g	lycerine mi	xtures with	MnSO ₄
c _M	s	ρ	η_s	β_s v 10 ⁻¹⁰	U Ms ⁻¹	$[\alpha / f^2]_{obs}$	$[\alpha / f^2]_{cla}$	$[\alpha / f^2]_{exc}$	τ v 10 ⁻¹¹
(w/w)		kg/m ³	Nsm ⁻²	$N^{-1}m^2$	1013	Nps ² m ⁻¹	Nps ² m ⁻¹	Nps ² m ⁻¹	x IU s
0.0	Α	1035.1	0.962	3.965	1560.8	48.58	6.433	42.14	3.841
	В	1058.2	1.238	3.688	1600.7	54.64	7.507	47.13	4.430
	С	1077.4	1.841	3.429	1645.2	70.19	10.099	60.09	5.850
0.1	Α	1037.2	0.963	3.909	1570.3	52.42	6.316	46.10	4.170
	В	1060.5	1.241	3.633	1610.8	59.24	7.368	51.87	4.834
	С	1080.4	1.842	3.366	1658.1	74.35	9.843	64.51	6.245
0.2	Α	1039.5	0.965	3.890	1572.4	52.60	6.289	46.31	4.190
	В	1062.8	1.245	3.609	1614.6	60.40	7.329	53.07	4.941
	С	1082.1	1.860	3.332	1665.3	77.24	9.796	67.44	6.516
0.3	Α	1040.2	0.967	3.863	1577.5	51.92	6.232	45.68	4.149
	В	1062.5	1.245	3.582	1620.8	60.40	7.248	53.15	4.959
	С	1083.4	1.861	3.320	1667.2	75.62	9.755	65.86	6.386
0.4	Α	1041.8	0.967	3.851	1578.6	52.70	6.210	46.48	4.216
	В	1063.1	1.246	3.563	1624.8	61.80	7.191	54.60	5.086
	С	1084.9	1.863	3.301	1671.0	78.64	9.864	68.95	6.657
0.5	Α	1042.1	0.968	3.843	1580.1	53.80	6.193	47.60	4.307
	В	1063.4	1.246	3.542	1629.3	62.12	7.130	54.98	5.127
	С	1085.4	1.863	3.292	1672.9	78.98	9.649	69.33	6.693
0.6	А	1043.1	0.968	3.812	1585.6	53.98	6.124	47.85	4.336
	В	1065.8	1.247	3.524	1631.5	62.38	7.087	55.29	5.158
	С	1087.6	1.868	3.276	1675.1	79.84	9.616	70.22	6.775

 Table – 1

 Ultrasonic velocity and absorption values for water - glycerine mixtures with MnSC

 $c_{M} = \text{concentration}; \quad s = \text{solution}; \quad \rho = \text{density}; \quad \eta_{s} = \text{shear viscosity}; \quad \beta_{s} = \text{adiabatic compressibility}; \quad u = \text{velocity}; \quad [\alpha / f^{2}]_{obs} = \text{observed absorption}; \quad [\alpha / f^{2}]_{cl} = \text{classical absorption}; \quad [\alpha / f^{2}]_{ex} = \text{excess absorption}; \quad \tau = \text{relaxation time};$

 Table – 2

 Ultrasonic velocity and absorption values for water - glycerine mixtures with VOSO4

childbonne		, 010 010 j	und abbol prion		fundes for mater g		ij een me minteur es with		10004
c _M	s	ρ	η_s	β_s x 10 ⁻¹⁰	U	$[\alpha / f^2]_{obs}$	$[\alpha / f^2]_{cla}$	$[\alpha / f^2]_{exc}$	τ x 10 ⁻¹¹
(w/w)		kg/m ³	Nsm ⁻²	$N^{-1}m^2$	ms ⁻¹	Nps ² m ⁻¹	Nps ² m ⁻¹	Nps ² m ⁻¹	s IO
0.0	Α	1035.1	0.962	3.965	1560.8	48.58	6.433	42.14	3.841
	В	1058.2	1.238	3.688	1600.7	54.64	7.507	47.13	4.430
	С	1077.4	1.841	3.429	1645.2	70.19	10.099	60.09	5.850
0.1	Α	1039.8	0.964	3.930	1564.2	51.28	6.380	44.89	4.063
	В	1062.1	1.241	3.626	1611.4	59.68	7.348	52.33	4.871
	С	1080.9	1.846	3.376	1655.1	74.88	9.916	64.96	6.278
0.2	Α	1040.7	0.967	3.916	1566.4	52.98	6.361	46.61	4.204
	В	1063.3	1.242	3.607	1614.6	60.48	7.303	53.17	4.947
	С	1082.2	1.849	3.361	1658.1	76.01	9.864	66.15	6.385
0.3	Α	1042.1	0.968	3.884	1571.8	53.92	6.295	47.62	4.293
	В	1065.0	1.243	3.585	1618.3	62.22	7.252	54.96	5.101
	С	1083.8	1.850	3.341	1661.6	78.48	9.792	68.68	6.606
0.4	Α	1043.9	0.969	3.872	1572.9	52.80	6.283	46.51	4.207
	В	1066.7	1.245	3.571	1620.1	62.01	7.224	54.78	5.089
	С	1085.1	1.851	3.321	1665.6	79.02	9.715	69.30	6.668
0.5	Α	1045.4	0.971	3.860	1574.1	54.18	6.265	47.91	4.320
	В	1068.2	1.247	3.552	1623.4	63.88	7.182	56.69	5.253
	C	1087.1	1.852	3.310	1666.9	81.02	9.680	71.33	6.841
0.6	A	1047.1	0.971	3.834	1578.1	55.80	6.212	49.58	4.461
	В	1070.4	1.248	3.533	1625.9	64.19	7.141	57.05	5.288
	С	1088.8	1.853	3.296	1669.2	82.81	9.631	73.17	7.003

 $c_{M} = \text{concentration}; \quad s = \text{solution}; \quad \rho = \text{density}; \quad \eta_{s} = \text{shear viscosity}; \quad \beta_{s} = \text{adiabatic compressibility}; \quad u = \text{velocity}; \quad [\alpha / f^{2}]_{obs} = \text{observed absorption}; \quad [\alpha / f^{2}]_{cl} = \text{classical absorption}; \quad [\alpha / f^{2}]_{ex} = \text{excess absorption}; \quad \tau = \text{relaxation time};$

Table 3 Spin Hamiltonian values for MnSO4 in water - glycerine mixtures at various concentrations

c _M	S	А	g
(w/w)		(mT)	
0.1	Α	9.18	2.003
	В	9.18	2.006
	С	9.18	2.006
0.2	Α	9.18	2.006
	В	9.18	2.006
	С	9.18	2.006
0.3	Α	9.29	2.004
	В	9.18	2.006
	С	9.18	2.006
0.4	Α	9.18	2.006
	В	9.18	2.006
	С	9.29	2.006
0.5	Α	9.18	2.006
	В	9.18	2.005
	С	9.18	2.006
0.6	Α	9.18	2.006
	В	9.18	2.006
	С	9.18	2.005

Table 4

Spin Hamiltonian values for VOSO₄ in water - glycerine mixtures at various concentrations

c _M	s	А	g
(w/w)		(mT)	
0.1	Α	11.16	1.971
	В	11.16	1.971
	С	11.16	1.973
0.2	Α	11.18	1.971
	В	11.18	1.971
	С	11.18	1.973
0.3	Α	11.36	1.972
	В	11.36	1.972
	С	11.36	1.973
0.4	Α	11.24	1.971
	В	11.24	1.971
	С	11.36	1.971
0.5	Α	11.30	1.973
	В	11.24	1.972
	С	11.36	1.973
0.6	Α	11.16	1.965
	В	11.16	1.971
	С	11.16	1.973

5.H. S. Frank and A. L. Robinson, J. Chem. Phys. 8 (1940) 933

6.H. S. Frank and M. W. Evans, J. Chem. Phys. 13 (1945) 507

7.R. W. Gurney, Ionic Processes in Solutions, McGraw Hill, New York, (1953)

8.J. H. Wang, J. Phys. Chem. 58 (1954) 686

- 9.R. Pragasam, M. Phil., Thesis, Pondicherry University, (1988) 10.S. G. Modak, P. L. Khare, and C. Mandey, Ind. J. Pure Appl. Phys. 10 (1972) 293
- 11. F. H. Willis, J. Acoust. Soc. Amer. 57-B (1967) 1
- 12.M. J. Blandamer, Introduction to Chemical Ultrasonics, Academic Press, London, (1973)
- 13.G. Ravichandran, S. Adilakshmi, A. Srinivasa Rao and T. K. Nambinarayanan, Acustica 75 (1991) 224
- 14.G. Ravichandran, A. Srinivasa Rao and T. K. Nambinarayanan, Ind. J. Pure Appl. Phys. 29 (1991) 792
- 15.K. Srinivasa Manja and A. Srinivasa Rao, Pramana 26 (1986) 459
- 16.A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Oxford, Clarendon Press (1970)

17.H. A. Kuska, M. T. Rogers, E. T. Kaiser and L. Kevan, (Eds.), Radical ions, Interscience, New York (1968)

18.B.R. McGarvey, Transition Metal Chemistry, ed. R.L. Carlin, 3 (1966) 89

19.V.S.X. Anthonisamy, M. Velayutham and R. Murugesan, Physica B 13 (1999) 262

20.R. Murugesan, A. Thamaraichelvan, A. M. Franklin and V. Ramakrishnan, Molec. Phys. 79 (1993) 663

21.B. Venkataraman, Ind. J. Pure and Applied Phys. 34 (1990) 273

22.P. Sambasiva Rao and S. Subramanian, Molec. Phys. 54 (1985) 429

23.M. A. M. Abuyoussef, A. Escuer, D. Gatteschi and M. A. S. Goher, Inorg. Chem. 38 (1999) 5716

24.N. O. Gopal, K. V. Narsimhulu and J. Lakshmana Rao, J. Phys. Chem of Solids. 63 (2002) 295

25.T. Bodziony, I. E. Lipinski, J. Kuriata and W. Bednarski, Physica B 299 (2001) 70

26.K. V. Narasimhulu and J. L. Rao, Spectrochim. Acta (A) $53(14)\ (1997)\ 2605$

27.F. Celick, F. Koksal, I. Kartal and H. Gumus, J. Phys. Sci. 52(11) (1997) 765

28.S. Khasa, D. Prakash, V. P. Seth, S. K. Gupta and R. M. Krishna, Phil. Mag. B. 76 (6) (1997) 859