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THERMODYNAMIC STUDY OF 1, 3-DIARYL CARBAMIDES IN BINERY SOLVENT MIXTURES

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ABSTRACT
Viscosity measurement of 1,3-diaryl carbamides was carried out in different binary solvent mixtures. The study was implemented for several variations in percentage of binary solvents, variation in concentration of solute in binary solvents as well as variation in temperatures. Using above data relative viscosity, excess viscosity and thermodynamic parameters i.e. enthalpy, entropy and gibbs free energy have been computed. Thermodynamic parameters and viscosity have been calculated to interpret molecular interaction.
Keywords: Viscosity, thermodynamic parameters, molecular interaction.

INTRODUCTION

Viscosity implies resistance to flow. Viscometric property has been a sensitive tool for understanding interactions in solution. Viscosity measurement, like other transport properties of liquids provides useful information about solute-solute and solvent-solvent interactions in nonaqueous and aqueous solvents [1-3] . Many workers studies molecular interactions and thermodynamic study of ternary liquid mixture at different temperatures [4,5] . Pandey and Yasmin [6] have experimentally measured viscosities & densities of aqueous binary electrolyte solutions of different molalities at 298.15 K & reported relative viscosities, apparent molar volumes and free energy of activation. H. Iioukhani, M. Rezaei-sameti and H.A. Zarei[7] studied volumetric and viscometric studies of molecular interactions of the ternary system toluene + cyclohexane + n-hexane at 298.15 K. Palani et. al [8] studied volumetric and thermodynamic studies of molecular interaction in ternary liquids mixtures at 303, 308 and 313 k . Alireza Salabat, Abbas Mehrdad [9] studied viscometric and volumetric study of dilute aqueous solution of binary and ternary poly ethylene glycol / poly vinyl alcohol a systems at different temperature. Anwar Ali , Soghra Hyder, Saba Sabir, Dinesh Chand, Anil Kumar Nain [10] studied volumetric, viscometric and refractive index of behavior of α-amino acid and their groups contribution in aqueous D-glucose solution at different temperatures. Viscometric study of polymer mixtures studied by many researchers [11,12].
In present work an attempt has been made to determine viscosities and densities of substituted 1,3-diaryl carbamides in 80 % binary solvents at different concentrations at 318 ,310,304 ,300 k . The data obtained have been used to compute relative viscosity & viscosity β- coefficient which was further used to calculated thermodynamic parameters.

EXPERIMENTAL

1,4- dioxane , dimethyl sulphoxide , acetone of AR grade (purity 99.9 %) and doubly distilled water were used to prepare binary solvent mixtures. All weighings were made on electronic balance (± 0.001 g). The accuracy of density measurements was within ± 0.1 % kg m^{-3} . The viscosity measurements were carried out using thoroughly cleaned, dried Ostwald's viscometer. Temperature variation study was carried out by use of suite water bath and temperature variation was maintained with in ± 0.01^{o}C . The accuracy of viscosity measurement was within ± 0.11 % kg $^{-1}$s $^{-1}$. From the observations, relative and specific viscosities were calculated. From the temperature variations study, values of enthalpy change (Δ H) entropy change (ΔS) & free energy change (ΔG) were evaluated.

$$\text{Log } \eta_{r1} - \log \eta_{r2} = \Delta H/2.303\ (1/T_1 - 1/T_2)$$
$$\Delta S = (\Delta G - \Delta H)/T$$

RESULTS AND DISCUSSION

Different concentration of 1,3- diaryl carbamides were prepared in 80 % solvent-water mixture. Densities were measured with Pyknometer calibrated with doubly distilled water (0.996 x10 ^{3} Kg m^{-3} at 299 K). The viscosities of solutions were measured by clean dried Ostwald's viscometer. The viscosities determined for ternary mixtures of 1,3- diaryl carbamides + dioxane + water at different concentrations with the variation in temperature have been prepared in Table-1.

It would be seen from Table No-1 relative viscosities increases with increase in concentration of 1,3-diaryl carbamides. Which shows the simultaneous increase in interaction between solute-solvent. Viscosity study was carried out at 300, 304, 310 and 318 K. It reflects that with increase in temperature, viscosity decreases due to decrease in solute-solvent interaction.

Table-1: Determination of relative viscosities of different temperature.

System : 1,3 di-o-tolyl carbamide	Temp: 300k		
Relative viscosity (η_r) (Pa-s)			
Conc. (M)	DMSO-Water x10 ^{4}	Acetone -Water x10^3	Dioxane - Water x10 ^{4}
0.01	2.3352	5.8560	1.4479
0.02	2.3358	6.0960	1.5118
0.03	2.7460	6.2616	1.5612
0.04	2.8519	6.5193	1.6444
0.05	2.9000	6.7630	1.7521
Temp. :304K			
0.01	2.1677	5.4075	1.3396
0.02	2.2594	5.6754	1.4060
0.03	2.4043	5.6759	1.4157
0.04	2.5644	6.0394	1.5170
0.05	2.6730	6.5765	1.6069
Temp. :310K			
0.01	1.8197	4.7315	1.1091
0.02	2.1086	5.0118	1.1885
0.03	2.1527	5.2966	1.1803
0.04	2.2438	5.5590	1.3031
0.05	2.0796	5.7543	1.3677
Temp. :318K			
0.01	1.6061	4.4599	1.0282
0.02	1.6069	4.7067	1.0683
0.03	1.9040	4.8807	1.0929
0.04	1.9882	5.0942	1.1404
0.05	2.0582	5.3355	1.1730
System : 1,3 di-m-toyl carbamide	Temp : 300 k		
Conc. (M)	DMSO-Water x10 ^{4}	Acetone -Water x10^3	Dioxane - Water x10 ^{3}
0.01	2.1411	5.9404	8.0377
0.02	2.5214	6.1488	8.8231
0.03	2.6153	6.3141	9.3841
0.04	2.7149	6.4958	9.8074
0.05	2.7444	6.6870	1.0740 (x10^4)
Temp. :304K			
0.01	2.0230	5.5590	7.4473

0.02	2.3713	5.7147	8.2794
0.03	2.3550	5.9566	8.4527
0.04	2.6001	6.0813	8.8104
0.05	2.5822	6.3973	9.3756
		Temp. :310K	
0.01	1.8197	5.2239	6.6221
0.02	2.1379	5.2339	6.9502
0.03	2.2594	5.4450	7.2945
0.04	2.3388	5.4458	7.4989
0.05	2.4043	5.7147	8.2794
		Temp. :318K	
0.01	1.6698	4.7543	6.0070
0.02	2.0155	4.9482	6.0535
0.03	2.1217	5.1891	6.3520
0.04	2.2484	5.4413	6.5246
0.05	2.2979	5.7021	7.0139

System : 1,3-di- p- tolyl carbamide . Temp. : 300 K

Conc. (M)	DMSO-Water x10 ^{4}	Acetone -Water x10^{3}	Dioxane - Water x10 ^{4}
0.01	2.3400	6.0306	1.3663
0.02	2.5890	6.2447	1.4226
0.03	2.7589	6.5032	1.4672
0.04	2.8372	6.9910	1.5419
0.05	3.0936	7.3489	1.5874
		Temp. :304K	
0.01	2.1527	5.5590	1.2852
0.02	2.3713	5.7147	1.3396
0.03	2.6181	5.9156	1.3677
0.04	2.6546	6.5313	1.4554
0.05	2.9040	6.8548	1.5066
		Temp. :310K	
0.01	1.8197	5.0118	1.1721
0.02	2.1978	501168	1.1803
0.03	2.3067	5.3703	1.1803
0.04	2.4378	5.3333	1.3212
0.05	2.7478	6.4416	1.3583
		Temp. :318K	
0.01	1.7481	4.4089	1.0970
0.02	2.0390	4.5910	1.1413
0.03	2.2258	4.7875	1.1722
0.04	2.2955	5.1702	1.2127
0.05	2.6243	5.7874	1.2438

Table-2: Determination of thermodynamic parameters

System :- 1,3 di-o-toyl carbamide

In 80 % DMSO –Water			
Conc. (M)	$\Delta G(Jk^{-1}mol^{-1})$	ΔS (J mol^{-1})	ΔH ($Jk^{-1}mole^{-1}$)
0.01	- 15.9501	-6.4725	1984.0611
0.02	-13.9970	-6.4515	1979.5449
0.03	-17.3479	-6.3384	1941.2185
0.04	-14.3608	-6.2343	1912.0465
0.05	-15.5863	-5.9325	1817.5732
In 80 % Acetone -Water			
0.01	-11.9673	-4.7105	1443.5860
0.02	-11.6801	-4.4745	1370.9612
0.03	-9.4015	-4.3048	1320.7951
0.04	-11.4886	-4.2689	1307.6128
0.05	-10.0526	-4.0999	1256.8364
In 80 % Dioxane -Water			
0.01	-13.8285	-5.9169	1814.5218
0.02	-15.2225	-6.0056	1840.5202
0.03	-16.7735	-6.1726	1890.5642
0.04	-16.2756	-6.3313	1940.1200
0.05	-16.2182	-6.9347	2126.6254

System: 1,3 di-m-tolyl Carbamide

In 80 % DMSO -Water			
Conc. (M)	$\Delta G(Jk^{-1}mol^{-1})$	ΔS (J mol^{-1})	ΔH ($Jk^{-1}mole^{-1}$)
0.01	-11.7012	-4.5619	1400.2136
0.02	-9.7462	-4.1060	1261.0740
0.03	-8.6165	-3.8334	1177.8237
0.04	-9.9951	-3.4628	1061.7659
0.05	-7.5059	-3.2554	1000.0414
In 80 % Acetone -Water			
0.01	-9.5739	-3.8519	1180.6719
0.02	-8.3484	-3.7535	1151.5
0.03	-7.9846	-3.3921	1040.1826
0.04	-8.4250	-3.0660	938.9961
0.05	-6.5294	-2.7546	844.6449
In 80 % Dioxane -Water			
0.01	-12.4460	-5.0359	1543.6739
0.02	-15.1459	-6.5117	1996.9993
0.03	-17.2521	-6.7504	2068.6476
0.04	-18.5733	-7.0518	2160.4356
0.05	-19.1478	-7.3716	2258.6927

System :1,3 di-p-tolyl Carbamides

In 80 % DMSO -Water			
Conc. (M)	$\Delta G(Jk^{-1}mol^{-1})$	ΔS (J mol^{-1})	ΔH ($Jk^{-1}mole^{-1}$)
0.01	-11.9673	-5.3532	1642.1842
0.02	-11.4886	-4.1334	1265.7467
0.03	-10.1292	-3.7166	1138.3176
0.04	-9.3632	-3.6648	1123.0603
0.05	-8.6165	-2.8498	871.9860

In 80 % Acetone -Water			
0.01	-14.5523	-5.4204	1660.3619
0.02	-13.7289	-5.3217	1630.7017
0.03	-13.9779	-5.2992	1623.5002
0.04	-12.8481	-5.2170	1599.2106
0.05	-11.1057	-4.1337	1266.2350
In 80 % Dioxane -Water			
0.01	-10.3103	-3.7986	1163.4617
0.02	-11.1057	-3.8154	1167.8558
0.03	-9.1909	-3.8803	1189.8263
0.04	-8.9037	-4.1491	1273.1923
0.05	-10.3398	-4.2182	1293.0878

Viscosity is determined by strength of intermolecular force. When that force is more. Shear strength of liquid will be more and likewise the viscosity. When that force is small , shear strength of liquid is small and its viscosity will be low. Three types of Vanderwaal's interactions exists between liquid molecules as London forces, dipole-dipole interaction and hydrogen bonding. Water is polar solvent and exhibit hydrogen bonding but has weak London forces. With the addition of other solvent intramolecular forces develop which again changes on addition of solute. Hence due to variable solvent-solvent and solute-solvent interactions variable trends are observed in viscosity values.

The viscosities determined at different temperatures were used to evaluate thermodynamic parameters enthalpy change (Δ H), entropy change (Δ S), & free energy change (Δ G) presented in Table No-2. For DMSO- water and acetone -water with increase in concentration enthalpy change increases but entropy change decreases. But for the 1,4-dioxane-water system, with concentration increase, enthalpy & entropy change increases. This variations may be explained on the basis of polarity of solvents. Due to polar nature of acetone & DMSO they shows similar results and due to relativiely nonpolar nature of 1,4-dioxane results may show different nature . Negative value of Δ G represents release of energy with favorable interactions.

REFERENCES

1. K.J. Patil ,S.M. Manwatkar and S.S. Dondge*, Indian J. Chem.*,**33**, 4(1994).
2. F.Karia and Baluja , *Asian J. Chem*., **12**, 593(2000).
3. R.K. Wadi and V. Kakkar, *Indian J. Chem*., **39**, 598(2000).
4. A.S.Burghate, R.M.Kedar, P.B. Agrawal and M.L. Narwade *, Oriental J. Chem*., **16(3)**, 503(2000).
5. P.P. Deohate , P.B. Agrawal and B,N, Berad *, Asian J. Chem*., **15**, 1435(2003).
6. J.D. Panday and A. Yasmin , *Proc. Indian Acad. Sci*., **9**, 289(1997).
7. H.Iioukhani, M.Rezaei-Sameti, H.A. Zarei, *Thermodynamic Acta*,**438,** 9(2005).
8. A.N. Kannappan, S. Thirumaran and R. Palani*, Journal of Physical Science*, **20(2)**, 97(2009).
9. A. Salabat ,A. Mehrdad, *Journal of Molecular Liquids*,**157**, 57(2010).
10. A. Ali, S. Hyder , S.Sabir, D. Chand , A. Kumar Nain, *The Journal of Chemical Thermodynamics* , **38**,136(2006).
11. R. Garcia, O.Melad, C.M.Gomez , J.E. Figuerulo , A. Campos, *European Polymer Journal* **35**,47(1999).
12. R.K. Wanchoo, P.K. Sharma, *European Polymer Journal*, **39**,1481(2003).

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