STUDY THE VOLUMETRIC BEHAVIOURS AND VISCOSITY OF DIBROMO ACETIC ACID IN THIOUREA-WATER MIXTURES

Dunya Edan Al- Mammar
Department of Chemistry, College of science, University of Baghdad.

ABSTRACT

The investigation envolved determination of the partial molar volumes $\overline{V^o}$ at infinite dilution of the dibromo Acetic acid in the thiourea- water mixtures at five temperatures in the range 293.15-313.15 K and at five compositions in the range 5 to 30 percent by weight thiourea, the concentration of the acid in each solvent mixture covered the rang 10^{-3} to 0.4 mol dm^{-3}.

Densities and viscosities of thiourea-water have been measured at each temperature for all thiourea-water mixtures as well as for solutions of dibromo acetic acid. The concentration dependence of densities of dibromo acetic acid solution have been used to estimate the partial molar volumes.

The volumetric behaviours of thiourea-water have been investigated in terms of excess molar volume. The variation of the relative excess molar volume of mixture was found to be due to a volume contraction (negative ΔV)on mixing the constituents of the mixture. The results were rationalized in terms of the two models for liquied water; one maximally hydrogen-bonded and voluminous the other non-hydrogen-bonded and dense.

The thermodynamic activation parameters ($\Delta G^{\neq}, \Delta H^{\neq} and \Delta S^{\neq}$) for the ion flow in thiourea-water could be estimated from the dependence of viscosity on temperature . the presence of dibromo acetic acid in thiourea-water mixture did not influence sigificanlty the values of these thermodynamic activation parameters.

The dependence of dynamic viscosities (η_r) values on the concentrations (c) of dibromo acetic acid in thiourea-water have been determined, electrolytic solutions of moderate concentration generally have relative dynamic viscosities (η_r) which obey the empirical equation of Jone and Dole.

الخلاصة

يتضمن البحث ايجاد الحجم المولي الجزيئي عند التخفيف النهائي لحامض ثنائي بروميد حامض الخليك ($\overline{V^o}$) في مخاليط الثايويوريا والماء في خمس درجات حرارية من المدى (293.15 الى 313.15) كلفن وبأستخدام خمس تراكيب مختلفة من مخاليط الثايويوريا والماء تراوحت النسبة المئوية للثايويوريا فيها من 5 الى 30 % وتراوحت تراكيز الحامض في محاليلها (10^{-3} الى 0.4) مول للديسيمتر المكعب .وتم قياس الكثافة واللزوجة لكل مخلوط في كل درجة حرارية كما جرى قياس الكثافة واللزوجة لكافة محاليل الحامض في هذه المخاليط .وأمكن دراسة أعتمادية كثافة المحاليل على تراكيز الحامض الذائب فيها وأمكن دراسة السلوك الحجمي لمخاليط الثايويوريا مع الماء بدلالة الفيض الحجمي المولي وكان التغير الحاصل في فيض الحجم المولي النسبي للمخاليك ناجما عن التقلص الذي يحدث في الحجم (ΔV سالب) من جراء مزج مكونات المخلوط وفسرت النتائج بدلالة الانموذجين المعروفين لتركيب الماء الذي يكون الماء في احداهما في أقصى تآصر هيدروجيني وحجم كبير بينما أشتمل الاخر على مقدار أقل من التآصر الهيدروجيني وكثافة اكبر.

وساعدت هذه المعلومات في الحصول على معلمات التنشيط الثرموديناميكية للانسياب اللزوجي لمخلوط الثايويوريا والماء في غياب ووجود الحامض وذلك في دراسة اعتمادية اللزوجة على درجة الحرارة ان وجود حامض ثنائي برومو حامض الخليك لم يؤثر بشكل ملحوظ على قيم معلمات التنشيط .

وقد امكن ايجاد اعتماد قيم اللزوجة الدينمية على تركيز ثنائي بروميد حامض الخليك في مزيج الثايويوريا والماء و تبين ان المحاليل الالكتروليتية المتوسطة التركيز غالبا ما تمتلك لزوجة دينمية وغالبا ما تخضع لمعادلة جونزدول.

INTRODUCTION

It is necessary to investigate such physical properties of the solvent mixtures such as density and viscosity, accurate density measurements have also been performed of mixed solvent mixtures and the acid solution in order to determine the partial molar volume of dibromo acetic acid at infinite dilution.

Determination of the non-ideal behaviour of dibromo acetic acid solutions through the investigation of the excess molar volumes, temperature dependence of viscosity and the application of Jones and Dole equation.

(Wen and Saito, 1972) have studied partial molar volumes ($\overline{V}$) for some bromide salts in aqueous solution.

(Das and Ives, 1961) have investigated the subsistent effect of halogen atoms in acetic acid on the dissociation behaviour of the acid in water and in 50 wt$^{o}/_{o}$ ethylene carbonate-water mixture utilizing again electromotive force measurments.

(Shareef, 1994) has evoluted the physical properties of these mixed solvents, ethylene glycol-water, Glycerol water and urea-water.

Kundu and Mazumar,1973) have examined the thermodynamic behavior of HCL in different urea-water mixed solvents and in the same solvents, Saleh et al, 2000 the thermodynamic quantities of dichloro acetic acid from conductance measurement.

There is a dearth of knowledge concerning the volume behavior of dibromo acetic acid in thiourea-water mixture despite numerous similar investigations with strong electrolytes in such solvent mixtures (Saleh et al, 1990).

EXPERIMENTAL

Thiourea (NH_2CSNH_2) d 1.405 g.cm^{-3} and dibromo acetic acid (Br_2CHCO_2H) were of purum grade chemicals obtained from fluka with purities exceeding 99.6%, Doubly distilled water with electrolytic conductance of 4 x10^{-7} S cm^{-1} were used in the preparation of the thiourea-water mixtures. Five compositions of the thio-urea-water mixtures have been investigated in which the weight percentages wt% of thiourea were 5, 10, 15, 20 and 30. The composition of the solvent mixture was also expressed interms of mole fraction (X_2) of thiourea in the mixture.

The dibromo acetic acid solution in thiourea-water mixture at each composition have been prepared at nine concentrations (C) in the rang 0.005 to 0.4 mol dm^{-3}.

Densities were measured with an accuracy of $\pm$ 5x10^{-5} gm cm^{-3} using sprengel ostwal pycnometer of 25 ml capacity. Duplicate measurments were indentical within in $\pm$0.0003 gram per ml.

Viscosities were measured using ubbelohde suspended level viscometer (type c) with time of (85 S) for pure water at 25 C^{o} the viscometer was calibrated with doubly distilled water at each temperatures, the measuring was repeated several times, the uncertainty of the viscosity measurments was $\pm$0.1%.

The temperature of thiourea-water mixture or of the dibromo acetic acid solution was controlled with thermostat to within $\pm$0.01C^{o} .

All the solutions and solvent mixtures have been prepared by weight.

RESULT AND DISCUSSION

Densities (d) viscosities (η) of the solvent mixtures have been measured at five temperatures involving 293.15, 298.15, 303.15, 308.15 and 313.15K the data obtained are given in Table (1).

Table (1): Densities d (g cm-3) and viscosities η (cp) of thiourea-water mixtures for five compositions and at five temperatures. The composition of the solvent was expressed at weight percentages (wt%) and in terms of mole fraction (X2) of thiourea in the mixtures

W% thiourea	**X_2**	**293.15K**		**298.15K**		**303.15K**		**308.15K**		**313.15K**	
		d	**η**	**d**	**η**	**d**	**η**	**d**	**η**	**d**	**η**
5	0.0123	1.0130	1.061	1.011	1.008	1.010	0.950	1.007	0.822	1.0059	0.771
10	0.0256	1.029	1.13	1.025	1.02	1.024	1.981	1.020	0.901	1.0180	0.855
15	0.0400	1.046	1.270	1.039	1.075	1.034	1.002	1.0335	0.922	1.0330	0.877
20	0.0558	1.0561	1.242	1.051	1.16	1.049	1.009	1.047	0.969	1.0466	0.891
30	0.0730	1.088	1.931	1.078	1.353	1.0779	1.136	1.076	1.003	1.0753	0.909

Table (2 a, b) gives the measured density and viscosity for dibromo acetic acid in 15 wight percentage thiourea-water mixture ($X_2 = 0.04$). Generally densities and viscosities increased at constant temperature with increasing concentration of dibromo acetic acid Fig. (1 a, b).

Table (2): Densities (d) and viscosities (η) of dibromo acetic acid solution in thiourea-water mixture at five temperatures. The concentration (C) of the acid in the solutions ranged from 5 to 400 mol dm^{-3}

a = Densities

$C \times 10^3$ mol dm^{-3}	**(d) gm cm^{-3}**				
	T_1	**T_2**	**T_3**	**T_4**	**T_5**
5	1.0388	1.0368	1.0360	1.0341	1.0305
10	1.0392	1.0372	1.0365	1.0345	1.0310
40	1.0410	1.0389	1.0381	1.0360	1.0325
60	1.0420	1.0398	1.0390	1.0370	1.0335
80	1.0440	1.0415	1.0411	1.0382	1.0345
100	1.0450	1.0425	1.0420	1.0390	1.0355
200	1.0507	1.0482	1.0475	1.0440	1.0407
300	1.0565	1.0545	1.0540	1.0495	1.0460
400	1.0625	1.0598	1.0592	1.0550	1.0512

b = Viscosities

$C\times10^3$ mol dm^{-3}	$(\eta)(cp)$				
	T_1	T_2	T_3	T_4	T_5
5	1.31713	1.1550	1.0350	0.9500	0.8650
10	1.3012	1.1590	1.0411	0.9955	0.8699
40	1.3201	1.1611	1.0500	0.9600	0.8601
60	1.3250	1.1701	1.0551	0.9650	0.8700
80	1.3300	1.1780	1.0600	0.9700	0.8750
100	1.3350	1.1820	1.0650	0.9750	0.8811
200	1.3550	1.2150	1.0950	0.9850	0.8981
300	1.3850	1.2463	1.1251	0.9910	0.9211
400	1.4200	1.2750	1.1500	1.1200	0.9250

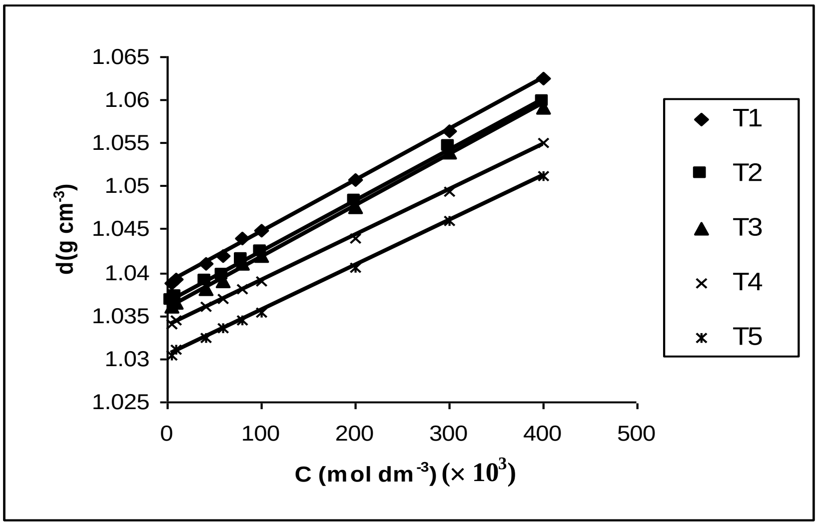


Fig (1-a): Variation of the densities (d) of dibromo acetic acid solutions in thiourea-water mixtures

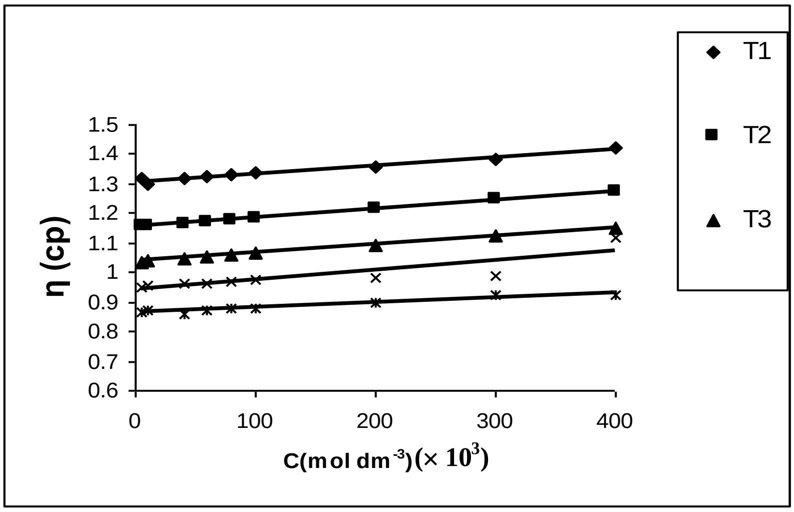


Fig (1-b): Variation of the viscosities (η) of dibromo acetic acid solution in thiourea-water mixtures

for all the systems; (Fig. 1a) the equation:

$$d = d_o + ac \qquad (1)$$

filled the data adequately. According to (Root, 1933):

$$a = \frac{M - d_o \overline{V^o}}{1000} \qquad (2)$$

Where (M) (g.mol^{-1}) and ($\overline{V^o}$) (cm^3 mol^{-1}) are the molecular mass and partial molar volume at infinite dilution of the electrolyte and d_o (gm.cm^{-3}) the density of the solvent mixture. partial molar volumes of dibromo acetic acid obtained from Eqn.(2) are given in Table (3).

Table (3): Partial molar volumes at infinite dilution ($\overline{V^o}$) of dibromo acetic acid solution in thiourea-water mixtures at five compositions and at five temperatures in the range 293.15K-313.15K.

wt% Thiourea	X_2	(cm^3 mol^{-1})$\overline{V^o}$				
		293.15K	298.15K	303.15K	308.15K	313.15 K
5	0.0123	72.011	70.66	71.89	77.06	72.97
10	0.0256	73.50	74.50	74.31	79.16	70.10
15	0.0400	71.70	71.51	69.72	78.00	69.70
20	0.0558	71.27	75.90	73.82	76.50	76.21
30	0.0730	77.70	67.98	77.23	77.72	78.60

Values of partial molar volumes at infinite dilution ($\overline{V^o}$) were close to an average value of (73) cm^3 mol^{-1} irrespective of temperature, acid concentration and solvent composition. The presence of solvent mixture give some reduction in the molar volume that of ideal molar volume for the acid .Which equal to 76.1 cm^3 mol^{-1} that obtained from density and molocular mass for the acid at 298.15K.

There is no similar data in the literature, to be compared with the estimated value of ($\overline{V^o}$) in the present work.

The volumetric behavior of thiourea-water mixture have been investigated interms of the exess molar volume (ΔV) (Aprano, 1974) as:

$$\Delta V = V_{\exp.} - V_{theo.} \qquad (3)$$

where ($V_{exp.}$) is the experimental molar volume in cm^3 defined by:

$$V_{\exp.} = (M_1 X_1 + M_2 X_2) / d_{12} \qquad (4)$$

and (V_{theor}) is the theoretical molar volume in cm^3 defined by:

$$V_{theo.} = M_1 X_1 / d_1 + M_2 X_2 / d_2 \qquad (5)$$

where (M) is the molecular mass of acomponent, (X) it's mole fraction and (d) it's density.

The subscripts 1, 2 and 12 denote the property of water, thiourea and their mixture respectively, in order to compare the results at different temperatures the relative excess molar volume in percent, was used.

$$\Delta V_{rel} = (\Delta V / V)100) \qquad (6)$$

The result are shown in Table (4) and Fig.(2) as a function of water mole fraction (X_1) at five different temperatures of thiourea-water mixtures. It can be noted that there is a volume contraction (negative ΔV) and further more the effect is greater at 313.15K than 293.15K. These result can be rationalized in terms of the two structure models for liquid water$^{(9)}$, one maximally hydrogen bounded and voluminous (Naim, 1972), the other non-hydrogen-bounded and dense. On this basis, the observed increasing packing density when the non-electrolyte thiourea is added to pure water must be ascribed to the destruction of the three-dimensional network of hydrogen-bonding present in pure liquid water. This explanation obtained at 313.15K than at 293.15K. In fact if we assume that the increase in temperature acts on the equilibrium between the two forms of water in the sense of promoting cluster distegration, we must expect a lower depolymerization of water by thiourea at the higher temperature. The increase in temperature acts on the equilibrium between the two forms of water.

Table (4): The experimental ($V_{exp.}$) and theoretical ($V_{theor.}$) molar volumes and relative excess molar volume $(-\Delta V)_{rel}$. of solvent mixtures at different temperatures

wt %	T (K)	V_{exp}.(cm^3)	V_{theor}.(cm^3)	$-\Delta V$	$(-\Delta V)_{rel.}$
0.05	293.15	18.338	18.403	0.065	0.3536
	298.15	18.413	18.463	0.05	0.2708
	303.15	18.4558	18.4928	0.037	0.2000
	308.15	18.5127	18.5367	0.24	1.2945
	313.15	18.5453	18.5628	0.0175	0.0943
0.1	293.15	18.7726	18.8636	0.091	0.483
	298.15	18.8379	18.9079	0.07	0.370
	303.15	18.8848	18.9438	0.059	0.3114
	308.15	18.9478	18.994	0.0462	0.243
	313.15	18.9797	19.0147	0.035	0.184
0.15	293.15	19.2358	19.3478	0.112	0.579
	298.15	19.3051	19.3951	0.09	0.464
	303.15	19.389	19.467	0.078	0.401
	308.15	19.4157	19.4809	0.0652	0.335
	313.15	19.4078	19.4828	0.0575	0.295

0.2	293.15	20.0028	20.1268	0.124	0.616
	298.15	20.0371	20.1571	0.12	0.595
	303.15	20.0711	20.1911	0.120	0.594
	308.15	20.1531	20.2483	0.0952	0.470
	313.15	20.1839	20.2477	0.0882	0.436
0.3	293.15	20.9152	21.0942	0.179	0.849
	298.15	20.9467	21.1157	0.169	0.800
	303.15	20.988	21.1491	0.1611	0.763
	308.15	21.0715	21.2121	0.1406	0.663
	313.15	21.1015	21.2417	0.1402	0.66

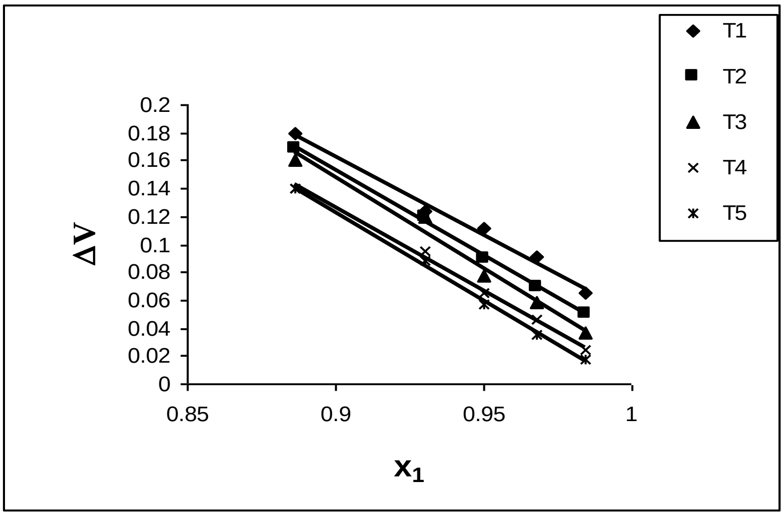


Fig.(2): Values of (ΔV) versus water mole fraction (X_1)in the solvent mixture for thiourea-water mixtures at five temperatures .

The dependence of viscosity on temperature may be described by Eyring's equation (Laider, 1950):

$$\eta = \frac{hN}{V}\exp\left(\frac{\Delta G^{\neq}}{RT}\right) \qquad (7)$$

Where V is the average molar volume of the solvent mixture at the absolute temperature (T) from Eqn.7 we can obtained the free energy of activation ($\Delta G^{\neq}$) for the viscous flow of a solvent such thiourea-water mixture by plotting (log η) as a function of (1/T) Table (5) and Fig.(3) values of the enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation may be obtained using the relation (Elsomogy,1978,1969).

$$\Delta S^{\neq} = -d(\Delta G^{\neq})dt \qquad (8)$$

and

$$\Delta H^{\neq} = \Delta G^{\neq} + T\Delta S^{\neq} \qquad (9)$$

Values of ($\Delta H^{\neq}, \Delta G^{\neq}, \Delta S^{\neq}$) for the viscous flow of the thiourea-water mixtures are present in Table (6) such data may be compared with those obtained for the solvent mixtures dissolving various amounts of dibromo acetic acid and similar experimental condition Table (6). The Gibbs free energy of activation ($\Delta G^{\neq}$) underwent some reduction with increasing the weight percentage of thiourea in the mixtures indicating a decrease in the resistance for the viscous flow of the solvent mixtures with the increasing proportion of thiourea in the mixture. In the presence (2) of acid values of $\Delta G^{\neq}$ increased by about 5 kJ.mol^{-1} at the relatively higher values of X_2. The flow thus encounter a greater resistance in the presence of the acid in the solvent mixture. The viscous & low of the solvent mixture is thus easier as compared with the flow of the acid solution.

Values of enthalpies of activation Table (6) increase with increasing values of X_2.

Table (5): (log η) values of thiourea-water mixtures from (0.05-0.3) wt% at 298.15K at five temperatures

(1/T) K^{-1}	**(log η)**				
	0.05wt%	**0.1wt%**	**0.15wt%**	**0.2wt%**	**0.3wt%**
0.003411	0.02268	-0.0296	-0.0825	-0.1204	-0.1618
0.00335	0.0421	-0.0237	-0.0704	-0.1227	-0.1545
0.00398	0.0676	0.035	-0.0489	-0.08	-0.14
0.00325	0.0861	0.0314	-0.025	-0.059	-0.1074
0.00319	0.145	0.0552	-0.0262	-0.025	-0.0752

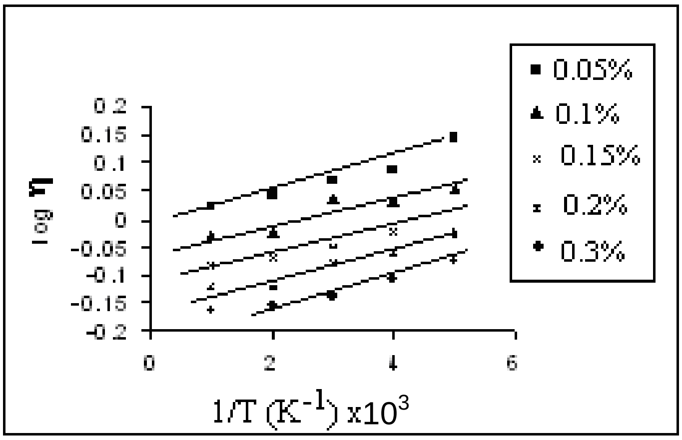


Fig.(3): (log η) values plotted against 1/T of thiourea-water mixtures from (0.05-0.3) wt%.

The greater alues of X_2 suggests that the gr in strength as the weight percentages of thiourea- in the thiourea-water mixture increases. The components of the solvent mixture becomes in a stronger bonding condition with increasing thiourea proportion as compared with the transition state mixture. A small increase in the degrees of freedom on passing from the ground to the transition-state in the activation process may be founded from the entropy of activation values ($\Delta S^{\neq}$) (Table (6)).

Table (5): Thermodynamic activation parameters ($\Delta G^{\neq}, \Delta H^{\neq} and \Delta S^{\neq}$) for the viscous flow of thiourea-water mixtures in the absence (1) and the presence (2) of dissolved dibromo acetic acid over the temperatures range (293.15-313.15 K) the composition of the solvent is expressed in weight percentage (Wt %)as well as in mole fraction (X_2) of thiourea in the thiourea-water mixtures

Wt % thiourea	X_2	$\Delta G^{\neq} / kJmol^{-1}$		$\Delta H^{\neq} / KJmol^{-1}$		$\Delta S^{\neq} / Jmol^{-1}K^{-1}$	
		(1)	(2)	(1)	(2)	(1)	(2)
5	0.0123	11.50	11.253	16.31	16.186	92.30	92.03
10	0.0256	9.170	14.995	15.10	14.3257	93.64	98.44
15	0.0400	9.80	14.199	16.62	14.8567	90.11	97.454
20	0.0558	10.60	12.673	16.72	15.778	92.52	95.426
30	0.0730	9.48	14.247	18.75	15.285	90.00	99.050

Electrolytic solution of moderate concentration generally have relative dyamic viscosities which obey the empirical equation of Jones and Dole (Erod, 1974) :

$$\eta_r = \frac{\eta}{\eta_o} = 1 + AC^{1/2} + BC \qquad (10)$$

Where η is the measured viscosity of the electrolyte solution , η_o is the viscosity of pure solvent at the same temperature , A and B are empirical constants independent of the concentration of the given system Eqn.10 may be by written as:

$$(\eta_r - 1)/C^{1/2} = A + BC^{1/2} \qquad (11)$$

Table (7) shows of $(\eta_r\text{-}1) / c^{1/2}$ value for dibromo acetic acid in the thiourea-water mixtures (0.05-0.3) wt% at 298.15K. By plotting $(\eta_r\text{-}1)/C^{1/2}$ as a function of $c^{1/2}$astraight line is obtained with a slop B and an intercept A Fig.(4).

Table (7): Values of $(\eta_r\text{-}1)/C^{1/2}$ and $C^{1/2}$ for dibromo acetic acid thiourea in the thiourea-water mixtures (0.05-0.3)wt% at 298.15K.

$C^{1/2}$	$(\eta_r - 1) / C^{1/2}$				
	0.05wt%	0.1wt%	0.15wt%	0.2wt%	0.3wt%
0.0707	-0.4915	-0.23	-0.4688	-0.42	-0.025
0.102	-0.4509	-0.17	-0.35	-0.33	0.025
0.2	-0.3490	-0.08	-0.261	-0.23	0.1085
0.2449	-0.2751	-0.025	-0.1018	-0.1889	0.1079
0.2828	-0.3574	-0.01	-0.1319	-0.12	0.15

0.3162	-0.1698	0.0196	-0.01919	-0.0563	0.4143
0.4472	-0.075	0.1056	0.101	0.0825	0.25
0.577	-0.0767	0.250	0.261	0.300	0.425
0.6325	0.1505	0.35	0.400	0.425	0.48

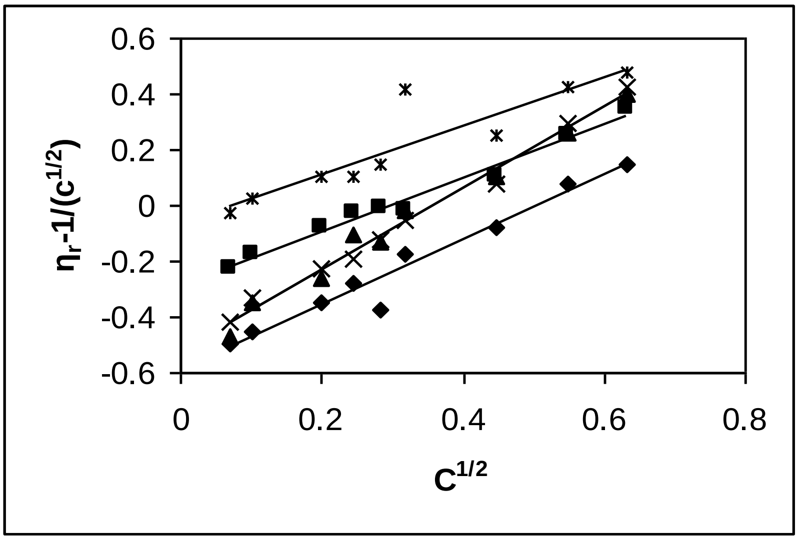


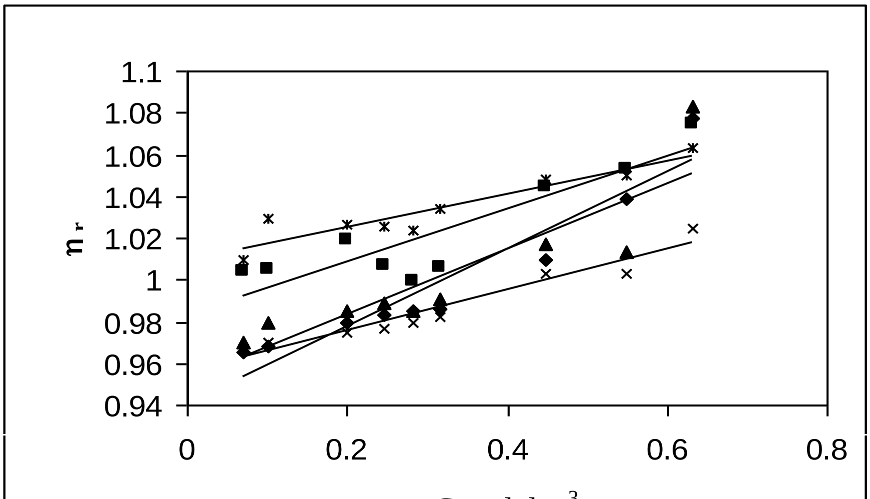
Fig.(4): Values of $(\eta_r-1)/C^{1/2}$ plotted versus $C^{1/2}$ for dibromo acetic acid in thiourea-water mixtures from 0.05wt%, 0.1wt%, 0.15wt%, 0.2wt%, 0.3wt% at 298.15K

Table (8) shows the values of Jones and Dole equation A,B.

Table (8): Constants of Jones and Dole of dibromo acetic acid in solvent mixtures at 298.15K

wt%	A	B
0.05	0.5853-	0.11635
0.1	0.2864-	0.9666
0.15	0.5237-	1.4566
0.2	0.5205-	1.4582
0.3	-0.6060	0.8725

The dependence of η_r values on the concentration (C) of the acid in the solvent mixture indicated in Fig(5) at constant temperature, the values η_r increased as the concentration of the dibromo acetic acid, this is likely to be due to the lower viscosities of the solvent mixture.



CONCLUSIONS

Densities and viscosities of thiourea-water mixture generally increased with increasing amount of thiourea in the mixture. This is reflected in the excess molar volumes implying non-ideal behaviour of thiourea mixture.

Densities of dibromo acetic acid in thiourea-water mixtures increased with increasing concentration of dibromo acetic acid in the solution. A similar trend was observed for the viscosity variation of dibromo acetic acid solution in the thiourea-water mixtures.

The concentration dependencies of the relative viscosities of dibromo solutions in thiourea-water mixtures followed Jones and Dole equation.

REFERENCES

- D. Aprano, Gazzetta Chemical Italiano, 104, 91, 1974.
- Das, N., and Ires, D.J.G, proc. Chem.. soc., 373, 1961.
- Erdoy-Gruj, T., Transport phenomena in aqueous solutions, (Adam Hilger, London, 1974), p.111.
- Elsomongy, M. M. (1978): Electrochim Acta, 23. 957.
- Elesomony, M. M. and fouda, A.S.J chem. Soc., Faraday trans. I, 77, 1169, 1981.
- Feakin, D. et al., J.chem. soc., Faraday trans.I, 82, 2195 and 82, 2207, 1986.
- Kundu, K.K, and Mazumar, K. J. chem.. soc, Faraday Trans, I, 69, 806, 1973.
- Laider, K.J (1950):chemical kinetics, MC Graw-hill Book co., New York.
- Naim, J.Ben, J.chem.phs.,56, 2864, 1972, 57, 3605, 1972.
- Root, W.C.J.Am. chem..soc., 55,850, 1933.
- Saleh, J. M. D. Mammar and N.A.Hikma, Iraqi J,chem.26,3,2000.
- Saleh, J. M.; N.Mustafa and N.A.. Hikmat, IraqiJ.Sci.,31,1, 1990.
- Shareef, K.M.; ph. D. thesis, Al-Nrhrain university, collage of science, July, 1994.
- Wen ,W.Y and Satio, S., J. phys. chem., 72, 1369, 1972.