

Interaction of ethylene glycols in aqueous Dimethyl sulfoxide Solutions at different Temperatures

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Abstract

Densities (ρ) and viscosities (η) of ethyleneglycole solutions in the range 0.1 to 0.35 mol dm⁻³ in 2% and 5% (w/w) Dimethylsulfoxide (DMSO)-water mixtures have been measured at different temperatures (298.15,303.15,308.15 and 313.15 K). From these experimental data, the apparent molar volume ϕ_v , limiting partial molar volume ϕ_v° , the slope S_v , Jones-Dole A and B-coefficients, Gibbs free energy of activation for viscous flow of solution ΔG^* , enthalpy ΔH^* and entropy ΔS^* were calculated. The results show strong ion-solvent interactions and weak ion-ion interactions and also indicate that the ethylene glycole acts as structure breakers.

Introduction

Acknowledge of chemical and physical properties of solvent systems two or more component liquids is often required in theoretical studies^{1,2} and for industrial and chemical processes at a wide range of temperatures⁽³⁻⁵⁾.

The intensive properties may include density, viscosity (or fluidity). Theoretical studies of binary mixtures reveal the importance of molecular interaction (hydrogen bonding, charge – transfer – complexes, dipole – dipole, dipole – induced dipole etc.) on the physical properties of these mixtures. Knowledge of the mixing properties is useful in design and simulation process, in the synthesis of pharmaceuticals, lacquers, resins, polymers, oxygenated fuels, and paints. Dimethyl-sulfoxide (DMSO) is a versatile dipolar aprotic solvent having relative dielectric constant $\epsilon = 46.50$ and dipole moment $M=4.06$ at 298.15 K⁽⁶⁾. It was used extensively in kinetic studies and electrochemistry and as a solvent for polymers.

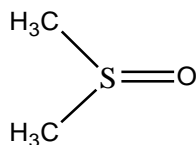
Aim of this study

The academic and technological importance of high density, high polar aprotic solvent dimethylsulfoxide lead us in this research to study the excess thermodynamic properties of the binary mixtures of this solvent with ethyleneglycole. The aims of this study are:

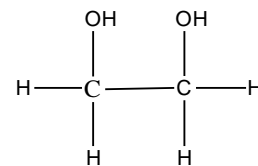
- i. To get a complete picture on the molecular interaction of these mixtures from their excess properties.

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- ii. To tabulate data which is necessary for chemical engineering design processes and polymer industry .



Methanesulfinylmethane
(dimethyl sulfoxide DMSO)
M.wt=78 gm/mol



Ethane-1,2-diol
(ethylene glycol)
M.wt=62.07gm/mol

Experimental

Dimethylsulfoxide obtained from Fluka AG (Buchs, Switzerland "spectral" grade material of stated purity >99 molpercent used without further purification . Ethyleneglycole obtained from Flukacompany is Analar and used without any further treatment .Solutions doubly distilled water (conductivity ~ 10⁻⁶ oh m⁻¹ cm⁻¹) were used . The concentration in these mixtures ranged from 0.1 -0.35 molar (mol dm⁻³) . The density ρ and the viscosity η were measured at different temperatures 298.15 , 303.15 , 308.15 and 313.15 K . The densities of ethyleneglycole solutions determined by PAAR Digital Meter , type DMA 60 in combination with DMA 602 remote cells .the volume of the solution which was needed for density measurements was 0.7 cm³ and the accuracy of the measurements lied within ± 0.5 × 10⁻⁵ g cm⁻³ of the density value .

The viscosities (η) of the various binary mixture were measured using Ostwald viscometer type (A). The uncertainty of the viscosity measurements was ± 0.1 % .

The thermostat which was used to maintain the temperature constant was of Haake refrigerated bath to which a circulator D1-G was incorporated . The constancy of each experimental temperature was to within ±0.01C° .

Result and Discussion :

The density and viscosity data measured for the solutions of ethylene glycole in aqueous dimethyl sulfoxide(DMSO + H₂ O) in Table (1) and in Figures 1,2 . The density data was used to compute apparent molar volumes φ_v , using the following relation

$$\phi_v = \frac{M}{\rho} - \frac{1000 (\rho - \rho_0)}{m \rho \rho_0} \text{-----(1)}$$

Where M is the molecular weight of solute and m is the molality

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[$m = 1/(\frac{\rho}{c} - \frac{M}{1000})$] of the solution ρ_o and ρ are the densities of solvent and solution respectively and C is the molar concentration . The results of ϕ_v° are tabulated in table (1) . The plot of ϕ_v against m in figure (3) shows a linear relationship where the slope equal S_v and the intercept , is ϕ_v° . Table (1) shows that the value of ϕ_v decrease with increase concentration of ethylene glycole but ϕ_v increase with increase DMSO content in the system suggesting that the solute solvent interaction increase with increasing DMSO % in solution⁽⁷⁾. The variation of apparent molar volumes ϕ_v with molar concentration can be adequately represented by equation (2)

$$\phi_v = \phi_v^\circ + S_v \text{-----}(2)$$

Where ϕ_v° is the apparent molar volume at infinite dilution and S_v is the experimental slope which also considered as the volumetric pairwise interactions coefficient⁽⁸⁻⁹⁾. The ϕ_v° reflects the presence of solute-solvent interactions , where aS_v , is indicated of the solute -solute interactions . Table (2) reveals that ϕ_v° Positive and increases with increasing temperatures, indicating the presence of solute-solvent interactions which increase as the temperature of solution increases The increase in ϕ_v° on going from 2% to 5% DMSO demonstrate the rising trend of solute solvent interaction. The S_v values are found to be negative . This illustrate weak solute – solute interactions and S_v values become more negative with increase in temperatures indicating an increased solute – solute interactions in solution and also shows the ethylene glycole behave as structure breakers⁽¹⁰⁾ . in fact negative S_v values are often obtained in solvent of high dielectric constant such as (DMSO – water) solvents⁽¹¹⁾ . The viscosity data was success fully analyzed according Jones – Dole equation⁽¹²⁻¹³⁾

$$\eta_r = \frac{\eta}{\eta_o} = 1 + A C^{1/2} + B C \text{-----}(3)$$

Where η and η_o are the viscosities of solution and solvent respectively , A and B viscosity coefficient which are empirical constant characteristic of give solute – solvent pair . A in equation (3) has been assigned to the electrostatic interaction of the solute particales with one another ,while the parameter B corresponds to the interaction between the solvent and the solute particles .Equation (3) may be written as :

$$(\eta_{r-1}) / C^{1/2} = A + B C^{1/2} \text{-----}(4)$$

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By plotting the left –hand term of equation (4) as a function of $C^{1/2}$, a straight line is obtained with a slop B and intercept A on the ordinate (table 2 and fig.4).This table and figures shows the lower in values of A and the grater values ofB for all ranges temperatures. this mean the ion – ion interactions become weak by increasing temperature while the ion – solvent become strong . this supports our earlier conclusion drawn from apparent molar ϕ_v° and S_v results . The activation free energy of viscose flow has been calculated by using the eyring relation ⁽¹⁴⁻¹⁵⁾ .

$$\Delta G^* = RT \ln \frac{\eta \bar{V}_{1,2}}{h N_A} \text{ -----(5)}$$

Where (ΔG^*) isthe free energy of activation (R) gas constant (T) absolute temperature (η) viscosity of solution (h) Planck's constant, (N_A) Avogadro number , ($\bar{V}_{1,2}$) is the molar volume of solution obtained from the following relation .

$$\bar{V}_{1,2} = (10^3 + mM_2) / \rho (\frac{10^3}{M_1} + m) \text{ ----- (6)}$$

Where M_1 and M_2 and the molecular weight for solvent and solute respectively , the values ΔG^* is calculated via equation (5) and given in table (3) .

Table (3) demonstrate that the values of ΔG^* increasing with increase the concentration of ethylene glycole and are grater values in 2% DMSO – water mixture from 5% DMSO – water mixture .The calculation of enthalpy , ΔH^* and entropy ΔS^* of activation of viscous flow was done using the following equation

$$\Delta G^* = \Delta H^* - T \Delta S^* \text{ ----- (7)}$$

The ΔH^* and ΔS^* are deduced from linear relation of ΔG^* vs. temperature . ΔH gives the structural information of the solute species and ΔS^* provides information regarding solute – solvent interactions⁽¹⁶⁾. The sign of $\partial B / \partial T$ is more straight forward indicator of the structure – making or – breaking ability of a solute rather than the sign or size of B – coefficient . The structure – makers will have negative $\partial B / \partial T$ values while structure – breakers will have a positive $\partial B / \partial T$ values ⁽¹⁷⁻¹⁸⁾ .The positive ($\partial B / \partial T$) values for ethylene glycole in two different percentage of DMSO – water

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mixtures indicate that ethylene glycole acts as a structure – breakers, this can see in (fig 5) .

Table 1:- Densities and viscosities (η) with calculated apparent molar volume, and the $\frac{\eta}{\eta^0} - (\phi_v)1/c$ of glycole in different percent w/w of aquaus dimethyl sulfoxide at different Temperatures

2%DMSO						5%DMSO				
C mol.L	m mol.kg ⁻¹	P g.cm ⁻³	η cp	ϕ^0 cm ³ mol ⁻¹	$\frac{\eta_{rel}-1}{\sqrt{c}}$	m mol.kg ⁻¹	P g.cm ⁻³	η cp	ϕ^0 cm ³ mol ⁻¹	$\frac{\eta_{rel}-1}{\sqrt{c}}$
0.1	0.10049	1.00128	0.92652	87.33718	0.17768	0.10023	1.00384	1.00199	93.02395	0.18108
0.15	0.15107	1.00220	0.94408	72.72463	0.19676	0.15073	1.00441	1.02333	78.78664	0.20599
0.2	0.20188	1.00310	0.96339	65.51846	0.21962	0.20138	1.00553	1.04111	68.93770	0.22034
0.25	0.25140	1.00430	0.98001	59.98929	0.23432	0.25120	1.00677	1.05988	62.55573	0.23669
0.3	0.30392	1.00572	0.99285	55.58980	0.24063	0.30330	1.00731	1.07555	60.61193	0.24626
0.35	0.35519	1.00711	1.01118	52.52519	0.25810	0.35495	1.00777	1.09882	59.45379	0.26824

298 K

2% DMSO						5% DMSO				
C mol.L	m mol.kg ⁻¹	P g.cm ⁻³	η cp	ϕ^0 cm ³ mol ⁻¹	$\frac{\eta_{rel}-1}{\sqrt{c}}$	m mol.kg ⁻¹	P g.cm ⁻³	η cp	ϕ^0 cm ³ mol ⁻¹	$\frac{\eta_{rel}-1}{\sqrt{c}}$
0.1	0.10054	1.00080	0.82059	100.5543	0.18607	0.10030	1.00319	0.90755	0.20580	99.27885
0.15	0.15110	1.00197	0.83793	73.48642	0.20969	0.15079	1.00407	0.92732	0.22790	80.90536
0.2	0.20199	1.00285	0.85506	66.41848	0.23102	0.20160	1.00444	0.94501	0.24387	74.25270
0.25	0.25290	1.00400	0.86924	60.91701	0.24322	0.25255	1.00542	0.96238	0.25889	67.83652
0.3	0.30415	1.00496	0.88455	58.6354	0.25810	0.30392	1.00570	0.97566	0.26479	65.87701
0.35	0.35546	1.00634	0.89992	60.88768	0.27250	0.35533	1.00670	0.99221	0.27798	62.43423

303 K

308 K

2% DMSO						5% DMSO				
C mol.L	m mol.kg ⁻¹	P g.cm ⁻³	η cp	ϕ^0 cm ³ mol ⁻¹	$\frac{\eta_{rel}-1}{\sqrt{c}}$	m mol.kg ⁻¹	P g.cm ⁻³	η cp	ϕ^0 cm ³ mol ⁻¹	$\frac{\eta_{rel}-1}{\sqrt{c}}$
0.1	0.10089	0.99730	0.71547	124.82469	0.19532	0.10072	0.99899	0.74996	139.42791	0.22009
0.15	0.15165	0.99840	0.73120	96.05622	0.21975	0.15152	0.99924	0.76661	111.84494	0.24102
0.2	0.20266	0.99926	0.74699	83.56842	0.24270	0.20254	0.99987	0.78233	96.16507	0.25886
0.25	0.25386	1.00028	0.75987	75.15835	0.25530	0.25378	1.00057	0.79566	86.48117	0.26955
0.3	0.30547	1.00071	0.77622	71.51127	0.27736	0.30534	1.00113	0.81222	80.48837	0.28918
0.35	0.35731	1.00125	0.79223	68.59325	0.29695	0.35722	1.00149	0.82555	76.77539	0.30004

313K

2% DMSO						5% DMSO				
C mol.L	m mol.kg ⁻¹	P g.cm ⁻³	η cp	ϕ^0 cm ³ mol ⁻¹	$\frac{\eta_{rel}-1}{\sqrt{c}}$	m mol.kg ⁻¹	P g.cm ⁻³	η cp	ϕ^0 cm ³ mol ⁻¹	$\frac{\eta_{rel}-1}{\sqrt{c}}$
0.1	0.10101	0.99619	0.66722	134.80417	0.20936	0.10099	0.99728	0.68322	154.17063	0.23004
0.15	0.15173	0.99785	0.68299	99.45772	0.23601	0.15166	0.99741	0.69992	122.58845	0.25553
0.2	0.20388	0.99817	0.69666	88.46202	0.25323	0.20279	0.99864	0.71225	101.20284	0.26458
0.25	0.25421	0.99895	0.70999	80.02952	0.26909	0.25407	0.99946	0.72766	90.03780	0.28504
0.3	0.30589	0.99935	0.72589	75.67146	0.29204	0.30542	0.99985	0.73997	84.05697	0.29549
0.35	0.35764	1.00034	0.73999	70.87873	0.30846	0.35755	1.00060	0.75432	78.69389	0.31166

Table 2 :-Jones- Dole coefficients A and B for ethylene glycole in varies DMSO –water mixtures at different Temperatures

Solu.	298 K	303 K	308 K	313 K
EG +H₂O +2% DMSO				
ϕ^0 cm ³ mol ⁻¹	95.051	101.79	132.81	142.45
S° cm ³ mol ⁻¹ /kg	-129.49	-138.95	-202.04	-222.23
A dm ³ mol ⁻²	0.095	0.079	0.089	0.087
B dm ³ mol ⁻¹	0.356	0.361	0.309	0.287
EG +H₂O +5% DMSO				
ϕ^0 cm ³ mol ⁻¹	99.644	105.08	151.54	166.75
S° cm ³ mol ⁻¹ /kg	-128.13	-131.85	-231.99	-265.57
A dm ³ mol ⁻²	0.140	0.128	0.127	0.087
B dm ³ mol ⁻¹	0.286	0.29	0.256	0.299

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Table 3:- Thermodynamic functions viscous flow ΔG^* , ΔH^* and ΔS^* of ethylene glycol in 2% and 5% of DMSO H₂O mixtures at different Temperatures

2% DMSO C mol/L	$\Delta G^* \text{ J.mol}^{-1}$				$\text{J.mol}^{-1} \Delta H^*$	$\text{J/mol.K} \Delta S^*$
	298 K	303 K	308 K	313 K		
0.00						
0.1	6338.24	6445.80	6561.13	6670.53	-291.6	22.24
0.15	6339.01	6447.86	6576.26	6672.13	-381.8	22.55
0.2	6342.82	6449.65	6579.88	6674.19	-358.0	22.48
0.25	6344.96	6451.79	6581.01	6676.13	-346.4	22.54
0.3	6346.49	6453.41	6583.44	6678.03	-356.2	22.49
0.35	6349.11	6455.99	6584.22	6679.40	-320.5	22.38
5% DMSO						
0.00						
0.1	6331.93	6439.80	6556.80	6667.69	-370.3	22.48
0.15	6332.56	6440.60	6557.11	6668.27	-365.8	22.47
0.2	6334.85	6442.67	6559.48	6669.02	-337.5	22.38
0.25	6336.89	6446.24	6560.66	6670.02	-301.9	22.27
0.3	6338.60	6448.55	6562.20	6672.81	-314.9	22.32
0.35	6342.50	6451.09	6564.26	6674.72	-272.9	22.19

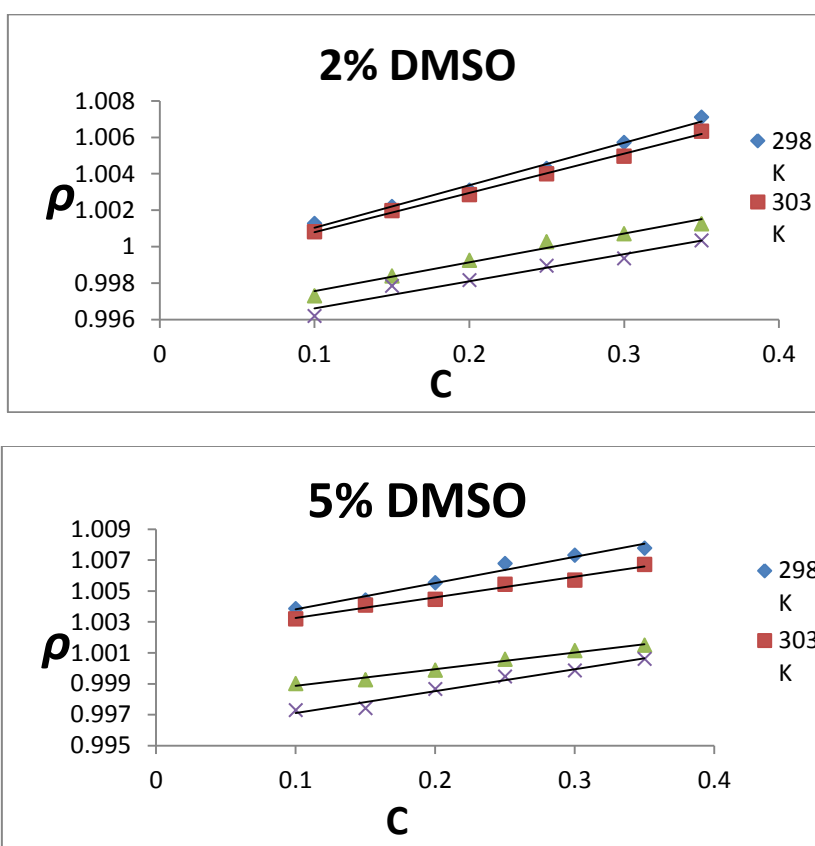


Figure 1: ρ vs. C for ethylene glycol in aqueous DMSO at different Temperatures

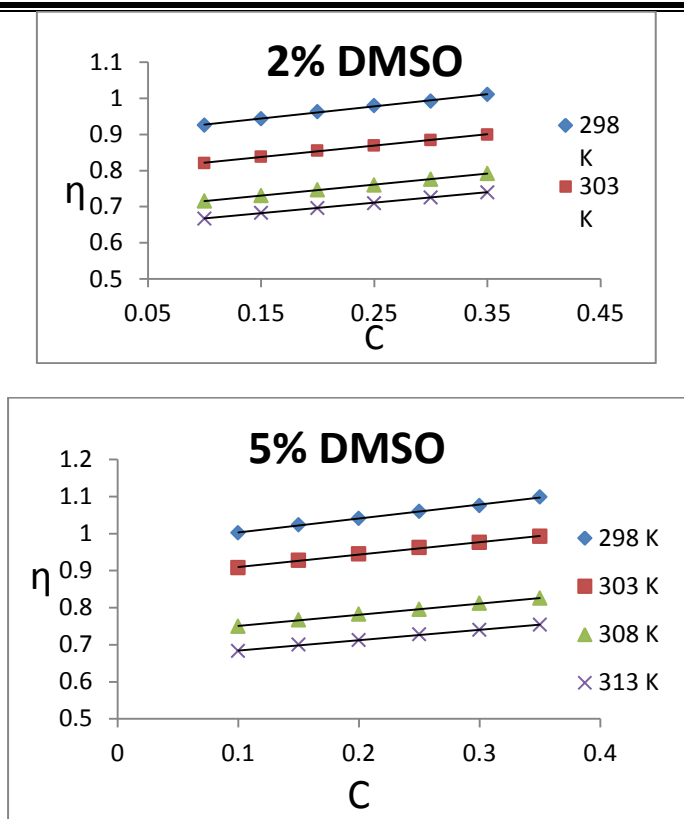


Figure 2: η vs. C for ethylene glycole in aquaus DMSO at different Temperatures

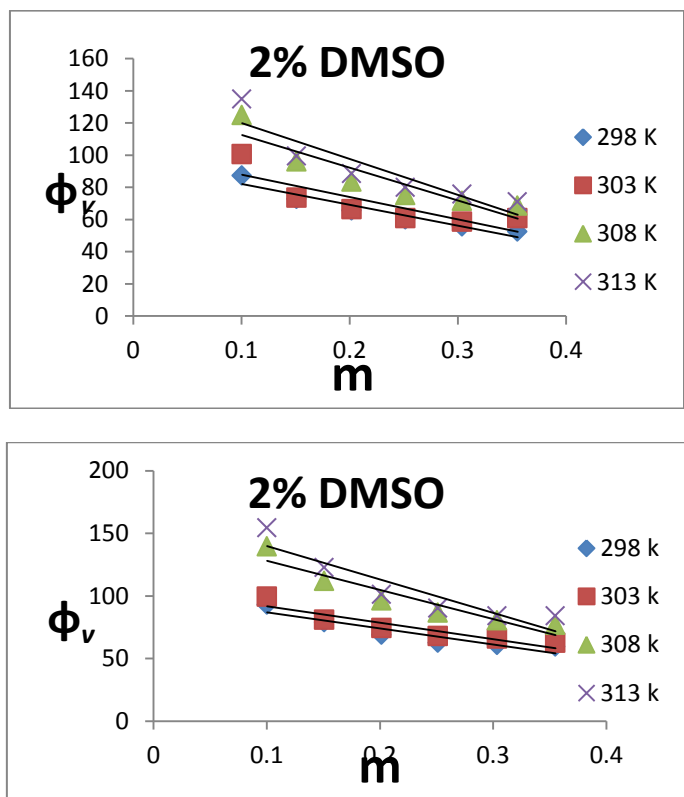


Figure 3: ϕ_v vs. m for ethylene glycole in aquaus DMSO.

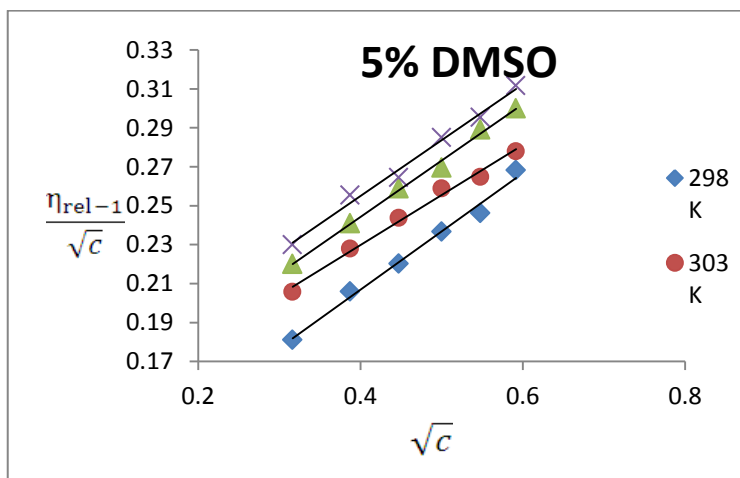
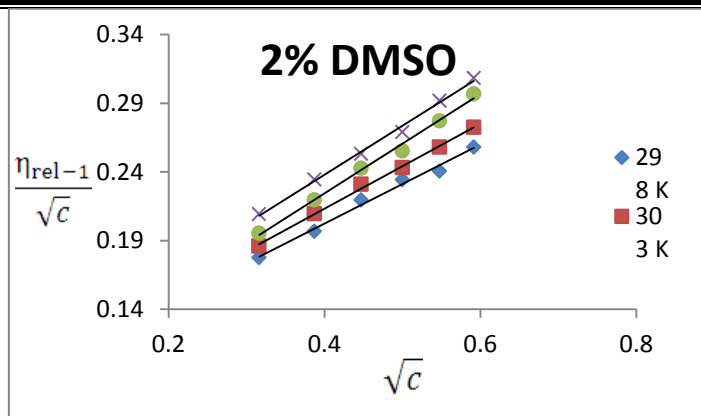


Figure 4 : $\frac{\eta_{rel}-1}{\sqrt{c}}$ against \sqrt{c} for ethylene glycole solutions at different temperatures

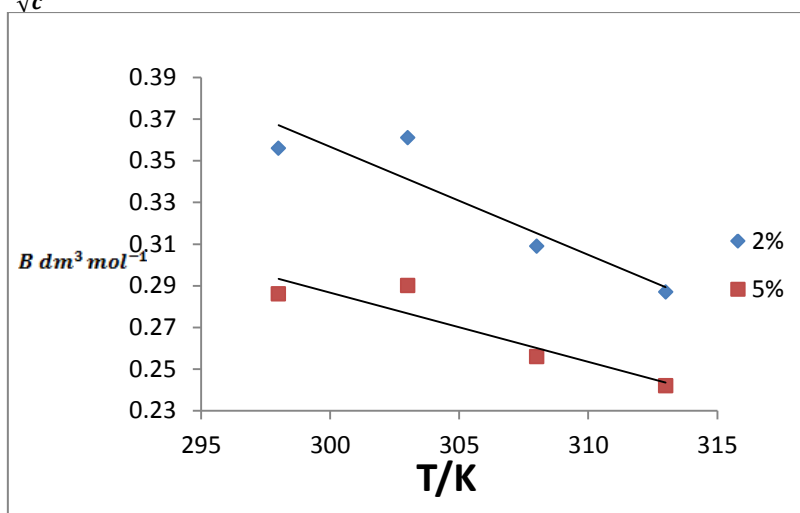


Figure 5 :- B- coefficient verses T for ethylene glycole in aquaus DMSO.

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تداخلات الاثيلين كلايكول في المحاليل المائية لثنائي مثيل سولفوكسايد عند درجات حرارة مختلفة

الملخص:

تضمنت هذه الدراسة قياسات الكثافة واللزوجة لمحاليل اثيلين كلايكول بست تراكيز مختلفة ضمن المدى 0.1 - 0.35 مول للديسمتر المكعب في مخلوطين مختلفي $\frac{w}{w}$ (2% - 5%) لمخاليط ثنائي مثيل سولفوكسايد مع الماء في أربع درجات حرارية مختلفة وضمن المدى 298.15 - 313.15 درجة مطلقة، استخدمت هذه النتائج لحساب الحجم المولاري الظاهري ϕ_v ، الحجم المولاري الظاهري المحدد ϕ_v° ، الميل S_v ، ومعاملا جونس - دول B,A ، طاقة كبس الحرة ΔG^* ، الانثالبي ΔH^* والانتروبي ΔS^* . أشارت النتائج إلى وجود تأثير قوي من نوع ايون - مذيب وضعيف من نوع ايون - ايون وبينت الدراسة أن سلوك الاثيلين كلايكول من نوع الهادم لتركيب المحلول المائي لثنائي مثيل سولفوكسايد .