Viscosity and Thermodynamic Properties of Alkali Metal Bromides in the Presence of Acetonitrile, 3-Hydroxypropionitrile and Acetonitrile + 3-Hydroxypropionitrile Mixture at Various Temperatures

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Abstract: Excess molar volume V_m^E, energy of activation ΔE_v, Gibbs energy change ΔG and entropy change ΔS have been investigated for this study density and viscosity measurements of Acetonitrile (AN), 3-hydroxypropionitrile (3-HPN) and 50% mixture of AN + 3-HPN and alkali metal bromides (Li,Na,K,Rb and Cs)Br in AN, 3-HPN and 50%AN+3-HPN over the concentration range (0.01 - 0.05 mol.dm^{-3}) at temperature range (298 to 323 K) were used. On the basis of Jones-Dole Equation the viscosity *B*-coefficient and the thermodynamic, activation parameters for viscous flow of solutions have been evaluated. The *B*-coefficient values of LiBr, NaBr , KBr, RbBr and CsBr are positive and decreases by increasing the temperature. The *B*-coefficient values are positive in protic and aprotic solvents. The positive values reveal that electrolytes behave as structure maker.

Keywords: Jones–Dole coefficient *A* and *B*, Excess molar volume, Energy of activation, Gibbs energy change and Entropy change.

INTRODUCTION

Several researchers determined the volumetric and viscometric behavior of electrolyte solutions in protic and aprotic solvents in order to investigate ion-solvent interactions [1-7]. The thermodynamic properties of binary mixtures of AN and 3-HPN have been extensively studied with the aim of investigating the interactions in solution phase with electrolytes LiBr, NaBr, KBr, RbBr and CsBr [8-11].

The alkali metal bromides were not completely soluble in AN except for LiBr. It was difficult to measure their viscosities and densities in AN. Mixtures of AN +3-HPN have great affinity to dissolve the alkali metal electrolytes because 3-HPN is a protic solvent and has great solubility property towards electrolytes [12].

The aim of this work is to report the experimental data of densities and viscosities of alkali metal bromides in AN, 3-HPN and in a 50% AN +3-HPN mixture at different temperatures to determine the activation and thermodynamic parameters like energy of activation ΔE_v, Gibbs energy change ΔG and entropy change ΔS. Results are discussed in terms of intermolecular interactions [13]. The excess molar volume is also reported for the binary solvent system.

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EXPERIMENTAL

Materials and Methods

AN 99.9% pure E. Merck and 3-HPN 98% pure Acros Organics New Jercey USA and were used without further purification. The densities and viscosities of AN, 3-HPN and 50% mixture of AN+3-HPN were measured at various temperatures as shown in Table **1**.

Alkali metal bromides such as LiBr (Riedel -de Haen 99%) NaBr (Scharlau 99.5%), KBr (Merck 99.5%), RbBr and CsBr(Acros Organics New Jercey) were used without further purification. Salts were stored in oven over well dried and desiccated to prevent the moisture.

Viscosities of solutions were measured using an Ostwald Viscometer type techniconominial with 0.1 (Cs/S) at different temperatures ranges from (298 to 323 K ± 0.1) with increase of 5K. The temperature was maintained constant throughout the course of experiment with the help of a thermostatic water bath type (circulator model YCM-01, Volt 230 AC, Hz 50, Amp 5). Densities were determined by relative density bottle with capacity of 10 ml by volume. A stopwatch (advance 85-quartz) having least count of 0.5 seconds was used for determination of time of flow of solutions.

Experimental work was accomplished to measure the viscosities and densities of AN, 3-HPN and 50%

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Table 1: Densities and Viscosities of AN, 3-HPN and 50% Mixture of AN+3-HPN at Various Temperatures

Temperature K	Density d (g.cm^{-3})		
	AN	3- HPN	AN+3-HPN
298	0.77634	1.03961	0.93482
303	0.77323	1.02763	0.93203
308	0.77136	1.02482	0.93006
313	0.76907	1.02152	0.92912
318	0.76824	1.01961	0.92794
323	0.76502	1.01664	0.92685
	Viscosity η (cp)		
298	0.333	3.572	0.9560
303	0.324	3.529	0.9534
308	0.316	3.493	0.9505
313	0.305	3.448	0.9492
318	0.296	3.410	0.9475
323	0.288	3.386	0.9458

mixture of AN + 3-HPN and alkali metal bromides in these solvents. Viscosities of alkali metal bromides in AN, 3-HPN and 50 % of AN+3-HPN were measured at all mentioned temperatures.

A known volume of alkali metal bromide solutions were introduced in to the viscometer by placing it in the thermostatic water bath having a constant circulation of water. Viscosities and densities were measured as a function of electrolytes concentrations and temperatures. Replicate experiments were performed for each solution. The experimental reproducibility of the viscosity measurements of each solution was ± 0.2%.

RESULTS AND DISSCUSSION

The densities and viscosities of AN, 3-HPN and 50% mixture of AN +3-HPN are showing slightly changes with temperature differences 5 K.

The viscosity was calculated from relationship.

$$\frac{\eta}{\eta_w} = \frac{dt}{d_w t_w} \quad (1)$$

where $d, \eta, t, d_w, \eta_w, t_w$ refer to the density, viscosity and time flow of solutions and water respectively. The viscosity of investigated solutions depends on the solute concentration and increases in a linear manner with concentrations [14].

The densities of alkali metal bromides solutions in AN, 3-HPN and 50% mixture of AN+3-HPNchanges slightly with the increase in temperature. The densities and viscosities of bromide electrolyte solutions in AN, 3-HPN and 50% mixture of AN+3-HPN were measured at different temperatures and reported in Tables **2**, **3** and **4** respectively. The results show that viscosity increases with increasing concentration of electrolytes and decreases with the increasing temperature.

The decrease in viscosity with increasing temperature is due to thermal vibration, which weakens the intermolecular forces of electrolyte solutions. The observed increase in viscosity with increasing salt concentration is due to the increase the intermolecular forces which cause to resist in flow process.

It is also observed that viscosities of solutions increased with the increase of electrolyte concentration which is a common feature in most non-aqueous solvents and also in the mixture of non-aqueous solvents [15].

The data of the viscosities of solutions obtained were used to study the solute-solute and solute-solvent interactions using the Jones-Dole equation [16].

$$\frac{\eta_{sp}}{\sqrt{C}} = A + B\sqrt{C} \quad (2)$$

where η_{sp} is the specific viscosity and *A* and *B* are equation coefficients that represent ion-ion and ion-solvent interactions of solution viscosity, respectively. The values of ion-ion and ion-solvent interactions are evaluated by intercept and slope of linear plot of $\frac{\eta_{sp}}{\sqrt{C}}$

Table 2: Densities and Viscosities of LiBr in AN at Various Temperatures

Temperature K	Concentration of LiBr (mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	Density d (g.cm^{-3})				
298	0.77742±0.0008	0.77801±0.0009	0.77923±0.0007	0.78091±0.0009	0.78124±0.0006
303	0.77601±0.0009	0.77760±0.0009	0.77832±0.0008	0.77903±0.0007	0.77961±0.0009
308	0.77131±0.0009	0.77422±0.0008	0.77660±0.0009	0.77751±0.0009	0.77822±0.0008
313	0.76911±0.0009	0.77101±0.0009	0.77313±0.0007	0.77582±0.0008	0.77653±0.0007
318	0.76292±0.0008	0.76482±0.0008	0.76721±0.0009	0.76943±0.0007	0.77294±0.0006
323	0.75424±0.0006	0.75651±0.0009	0.75802±0.0008	0.76423±0.0007	0.76504±0.00006
Viscosity η (cp)					
298	0.34182±0.0008	0.34703±0.0007	0.35169±0.0001	0.35509±0.0001	0.35977±0.0003
303	0.33477±0.0003	0.34074±0.0006	0.34606±0.0004	0.34994±0.0006	0.35486±0.0004
308	0.32805±0.0005	0.33521±0.0009	0.34691±0.0009	0.34507±0.0003	0.34869±0.0001
313	0.31901±0.0009	0.32295±0.0005	0.33085±0.0005	0.33187±0.0003	0.34307±0.0003
318	0.31075±0.0005	0.31633±0.0007	0.32005±0.0005	0.32367±0.0003	0.33721±0.0009
323	0.30646±0.0004	0.31155±0.0005	0.31594±0.0006	0.31848±0.0002	0.33698±0.0002

Table 3: Densities and Viscosities of Alkali Metal Bromide Salts in 3-HPN at Various Temperatures

Temperature K	Concentration (mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	LiBr Density d (g.cm^{-3})				
298	1.04002±0.00008	1.04131±0.00009	1.04253±0.00007	1.04342±0.00008	1.04403±0.00007
303	1.03963±0.00007	1.04082±0.00008	1.04144±0.00006	1.04293±0.00007	1.04355±0.00005
308	1.03914±0.00006	1.04024±0.00006	1.04101±0.00009	1.04181±0.00009	1.04272±0.00008
313	1.03851±0.00009	1.03970±0.00009	1.04060±0.00009	1.04125±0.00005	1.04193±0.00007
318	1.03803±0.00007	1.03922±0.00008	1.04012±0.00008	1.04075±0.00005	1.04131±0.00009
323	1.03742±0.00008	1.03854±0.00006	1.03945±0.00005	1.04032±0.00008	1.04091±0.00009
	LiBr Viscosity η (cp)				
298	3.62959±0.00001	3.67164±0.00006	3.701121±0.00009	3.71754±0.00006	3.74522±0.00008
303	3.60822±0.00008	3.65001±0.00009	3.68524±0.00007	3.71593±0.00007	3.74495±0.00005
308	3.58752±0.00008	3.64095±0.00005	3.67752±0.00008	3.71312±0.00008	3.74333±0.00007
313	3.56229±0.00001	3.63102±0.00008	3.65443±0.00007	3.71121±0.00009	3.74254±0.00006
318	3.55066±0.00004	3.61083±0.00007	3.65121±0.00009	3.70535±0.00005	3.74132±0.00008
323	3.54955±0.00005	3.56868±0.00002	3.60011±0.00009	3.69409±0.00001	3.7405±0.00005
	NaBr Density d (g.cm^{-3})				
298	1.04082±0.00008	1.04162±0.00008	1.04233±0.00007	1.04302±0.00008	1.04371±0.00009
303	1.04031±0.00009	1.04121±0.00009	1.04191±0.00009	1.04261±0.00009	1.04334±0.00006
308	1.04004±0.00006	1.04072±0.00008	1.04133±0.00007	1.04212±0.00008	1.04292±0.00008
313	1.03963±0.00007	1.04023±0.00007	1.04082±0.00008	1.04173±0.00007	1.04274±0.00006
318	1.03922±0.00008	1.03972±0.00008	1.04024±0.00006	1.04144±0.00006	1.04201±0.00009
323	1.03881±0.00009	1.03931±0.00009	1.03991±0.00009	1.04062±0.00008	1.04152±0.00008

(Table 3). Continued.

Temperature K	Concentration (mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	NaBr Viscosity η (cp)				
298	3.62944±0.00006	3.67152±0.00008	3.69522±0.00008	3.71842±0.00008	3.74514±0.00006
303	3.60689±0.00001	3.65461±0.00009	3.68491±0.00009	3.71791±0.00009	3.74482±0.00008
308	3.58741±0.00009	3.64084±0.00006	3.66432±0.00008	3.70901±0.00001	3.74321±0.00009
313	3.56018±0.00002	3.63794±0.00006	3.65332±0.00008	3.71019±0.00001	3.74242±0.00008
318	3.54152±0.00008	3.61001±0.00009	3.64313±0.00007	3.70078±0.00002	3.74121±0.00009
323	3.53964±0.00006	3.54001±0.0001	3.56236±0.00004	3.62193±0.00007	3.74096±0.00004
	KBr Density d (g.cm^{-3})				
298	1.04133±0.00007	1.04202±0.00008	1.04292±0.00008	1.04381±0.00009	1.04512±0.00008
303	1.04094±0.00006	1.04162±0.00008	1.04241±0.00009	1.04331±0.00009	1.04473±0.00007
308	1.04032±0.00008	1.04101±0.00009	1.04192±0.00008	1.04272±0.00008	1.04421±0.00009
313	1.03981±0.00009	1.04052±0.00008	1.04144±0.00006	1.04224±0.00006	1.04364±0.00006
318	1.03951±0.00009	1.04003±0.00007	1.04091±0.00009	1.04183±0.00007	1.04312±0.00008
323	1.03912±0.00008	1.03941±0.00009	1.04052±0.00008	1.04131±0.00009	1.04271±0.00009
	KBr Viscosity η (cp)				
298	3.63356±0.00004	3.66281±0.00009	3.69548±0.00002	3.71969±0.00001	3.74541±0.00009
303	3.61018±0.00002	3.65019±0.00001	3.68521±0.00009	3.71811±0.00009	3.74512±0.00008
308	3.58987±0.00006	3.64101±0.00009	3.67096±0.00004	3.71731±0.00009	3.74376±0.00004
313	3.56373±0.00007	3.63121±0.00009	3.65359±0.00001	3.71639±0.00001	3.74269±0.00001
318	3.54499±0.00001	3.61099±0.00001	3.64338±0.00002	3.71049±0.00001	3.74151±0.00009
323	3.54999±0.00001	3.54766±0.00004	358213±0.00007	3.63508±0.00002	3.7414±0.00006
	RbBr Density d (g.cm^{-3})				
298	1.04012±0.00008	1.04291±0.00009	1.04441±0.00009	1.04591±0.00009	1.04622±0.00008
303	1.03972±0.00008	1.04253±0.00007	1.04402±0.00008	1.04542±0.00008	1.04591±0.00009
308	1.03921±0.00009	1.04214±0.00006	1.04371±0.00009	1.04514±0.00006	1.04534±0.00006
313	1.03873±0.00007	1.04173±0.00007	1.04313±0.00007	1.04473±0.00007	1.04492±0.00008
318	1.03811±0.00009	1.04121±0.00009	1.04261±0.00009	1.04421±0.00009	1.04441±0.00009
323	1.03773±0.00007	1.04092±0.00008	1.04212±0.00008	1.04322±0.00008	1.04402±0.00008
	RbBr Viscosity η (cp)				
298	3.62902±0.00008	3.67022±0.00008	3.69411±0.00009	3.71606±0.00004	3.73802±0.00008
303	3.60599±0.00001	3.65326±0.00004	3.68251±0.00009	3.71528±0.00002	3.73569±0.00001
308	3.58624±0.00006	3.63898±0.00002	3.66228±0.00002	3.71363±0.00007	3.73325±0.00005
313	3.55999±0.00001	3.62699±0.00001	3.65214±0.00006	3.71025±0.00005	3.73112±0.00008
318	3.53999±0.00001	3.59685±0.00005	3.64236±0.00004	3.69056±0.00004	3.72999±0.00001
323	3.53459±0.00001	3.56406±0.00004	3.57614±0.00006	3.65009±0.00001	3.72632±0.00008
	CsBr Density d (g.cm^{-3})				
298	1.04242±0.00008	1.04302±0.00008	1.04483±0.00007	1.04641±0.00009	1.04762±0.00008
303	1.04192±0.00008	1.04265±0.00005	1.04445±0.00005	1.04571±0.00009	1.04712±0.00008
308	1.04121±0.00009	1.04201±0.00009	1.04383±0.00007	1.04522±0.00008	1.04664±0.00006
313	1.04073±0.00007	1.04153±0.00007	1.04334±0.00006	1.04484±0.00006	1.04622±0.00008
318	1.04032±0.0008	1.04114±0.00006	1.04271±0.00009	1.04433±0.00007	1.04574±0.00006
323	1.03974±0.00006	1.04072±0.00008	1.04222±0.00008	1.04385±0.00005	1.04533±0.00007

(Table 3). Continued.

Temperature K	Concentration (mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	CsBr Viscosity η (cp)				
298	3.62821±0.00009	3.66956±0.00004	3.69321±0.00009	3.71523±0.00007	3.72812±0.00008
303	3.60456±0.00004	3.65221±0.00009	3.68142±0.00008	3.71412±0.00008	3.72419±0.00001
308	3.58536±0.00004	3.63759±0.00001	3.66134±0.00006	3.71235±0.00005	3.72399±0.00001
313	3.55839±0.00001	3.62538±0.00002	3.65114±0.00006	3.70896±0.00004	3.72006±0.00004
318	3.53846±0.00004	3.59536±0.00004	3.64111±0.00009	3.68892±0.00008	3.71989±0.00001
323	3.53343±0.00007	3.56169±0.00001	3.57054±0.00006	3.66323±0.00007	3.71625±0.00005

Table 4: Densities and Viscosities of Alkali Metal Bromide Salts in 50% Mixture of AN +3-HPN at Various Temperatures

Temperature K	Concentration(mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	LiBr Density d (g.cm^{-3})				
298	0.94561±0.00009	0.94602±0.00008	0.94632±0.00008	0.94683±0.00007	0.94712±0.00008
303	0.94402±0.00008	0.94431±0.00009	0.94471±0.00009	0.94502±0.00008	0.94521±0.00009
308	0.94293±0.00007	0.94323±0.00007	0.94363±0.00007	0.94394±0.00006	0.94414±0.00006
313	0.93961±0.00009	0.93994±0.00006	0.94014±0.00006	0.94041±0.00009	0.94072±0.00008
318	0.93552±0.00008	0.93572±0.00008	0.93602±0.00008	0.93633±0.00007	0.93673±0.00007
323	0.93214±0.00006	0.93241±0.00009	0.93271±0.00009	0.93292±0.00008	0.93311±0.00009
	LiBr Viscosity η (cp)				
298	0.96376±0.00004	0.97029±0.00001	0.97622±0.00008	0.98216±0.00003	0.98798±0.00002 0.98798±0.00002
303	0.96209±0.00001	0.96861±0.00007	0.97464±0.00006	0.98099±0.00001	0.98722±0.00008
308	0.96026±0.00004	0.96696±0.00004	0.97329±0.00007	0.98033±0.00007	0.98609±0.00001
313	0.95919±0.00001	0.96674±0.00006	0.97422±0.00008	0.97931±0.00009	0.98541±0.00009
318	0.95817±0.00007	0.96602±0.00008	0.97361±0.00009	0.97922±0.00008	0.98471±0.00009
323	0.95802±0.00008	0.96303±0.00007	0.96739±0.00001	0.97419±0.00001	0.98012±0.00008
	NaBr Density d (g.cm^{-3})				
298	0.94592±0.00008	0.94621±0.00009	0.94672±0.00008	0.94712±0.00008	0.94731±0.00009
303	0.94421±0.00009	0.94464±0.00006	0.94493±0.00007	0.94534±0.00006	0.94552±0.00008
308	0.94312±0.00008	0.94363±0.00007	0.94391±0.00009	0.94423±0.00007	0.94444±0.00006
313	0.93991±0.00009	0.94011±0.00009	0.94024±0.00006	0.94065±0.00005	0.94093±0.00007
318	0.93584±0.00006	0.93591±0.00009	0.93633±0.00007	0.93651±0.00009	0.93692±0.00008
323	0.93242±0.00008	0.93274±0.00006	0.93302±0.00008	0.93332±0.00008	0.93354±0.00006
	NaBr Viscosity η (cp)				
298	0.96330±0.0001	0.97017±0.00003	0.97611±0.00009	0.98204±0.00006	0.98756±0.00004
303	0.96151±0.00009	0.96786±0.00004	0.97451±0.00009	0.98071±0.00009	0.98611±0.00009
308	0.96019±0.00001	0.96593±0.00007	0.97317±0.00003	0.98021±0.00009	0.98599±0.00001
313	0.95889±0.00001	0.96641±0.00009	0.97409±0.00001	0.97918±0.00002	0.98529±0.00001
318	0.95801±0.00009	0.96511±0.00009	0.97348±0.00002	0.97909±0.00001	0.98458±0.00002
323	0.95781±0.00009	0.96369±0.00001	0.96832±0.00008	0.97475±0.00005	0.98001±0.00009

(Table 4). Continued.

Temperature K	Concentration(mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	KBr Density d (g.cm^{-3})				
298	0.94611±0.00009	0.94642±0.00008	0.94692±0.00008	0.94733±0.00007	0.94751±0.00009
303	0.94432±0.00008	0.94481±0.00009	0.94511±0.00009	0.94552±0.00008	0.94563±0.00007
308	0.94334±0.00006	0.94394±0.00006	0.94424±0.00006	0.94444±0.00006	0.94474±0.00006
313	0.94003±0.00007	0.94033±0.00007	0.94052±0.00008	0.94071±0.00009	0.94112±0.00008
318	0.93601±0.00009	0.93625±0.00005	0.93643±0.00007	0.93672±0.00008	0.93704±0.00006
323	0.93232±0.00008	0.93301±0.00009	0.93322±0.00008	0.93334±0.00006	0.93351±0.00009
	KBr Viscosity η (cp)				
298	0.96216±0.00004	0.96682±0.00008	0.97134±0.00006	0.97756±0.00004	0.98124±0.00006
303	0.96046±0.00004	0.96625±0.00005	0.97102±0.00008	0.97638±0.00002	0.98073±0.00007
308	0.95806±0.00004	0.96453±0.00007	0.97025±0.00005	0.97507±0.00003	0.97869±0.00001
313	0.95755±0.00005	0.96362±0.00008	0.96856±0.00004	0.97499±0.00001	0.97854±0.00006
318	0.95658±0.00002	0.96256±0.00004	0.96812±0.00008	0.97398±0.00002	0.97841±0.00009
323	0.95552±0.00008	0.96005±0.00005	0.96405±0.00005	0.96955±0.00005	0.97311±0.00009
	RbBr Density d (g.cm^{-3})				
298	0.94012±0.00008	0.94105±0.00005	0.94302±0.00008	0.94412±0.00008	0.94531±0.00009
303	0.93971±0.00009	0.94063±0.00007	0.94264±0.00006	0.94364±0.00006	0.94502±0.00008
308	0.93914±0.00006	0.94001±0.00009	0.94205±0.00005	0.94313±0.00007	0.94434±0.00006
313	0.93873±0.00007	0.93944±0.00006	0.94151±0.00009	0.94265±0.00005	0.94382±0.00008
318	0.93815±0.00005	0.93883±0.00007	0.94093±0.00007	0.94201±0.00009	0.94321±0.00009
323	0.93761±0.00009	0.93815±0.00005	0.94024±0.00006	0.94151±0.00009	0.94274±0.00006
	RbBr Viscosity η (cp)				
298	0.96321±0.00009	0.96791±0.00009	0.97315±0.00005	0.97891±0.00009	0.98345±0.00005
303	0.96121±0.00009	0.96731±0.00009	0.97211±0.00009	0.97725±0.00005	0.98266±0.00004
308	0.95926±0.00004	0.96563±0.00007	0.97165±0.00005	0.97615±0.00005	0.98149±0.00001
313	0.95841±0.00009	0.96492±0.00008	0.96995±0.00005	0.97584±0.00006	0.98099±0.00001
318	0.95736±0.00004	0.96382±0.00008	0.96936±0.00004	0.97482±0.00008	0.98066±0.00004
323	0.95692±0.00008	0.96122±0.00008	0.96611±0.00009	0.97132±0.00008	0.97552±0.00008
	CsBr Density d(g.cm^{-3})				
298	0.93492±0.00008	0.93601±0.00009	0.93771±0.00009	0.93861±0.00009	0.94002±00.0008
303	0.93411±0.00009	0.93555±0.00005	0.93714±0.00006	0.93814±0.00006	0.93941±0.00009
308	0.93374±0.00006	0.93512±0.00008	0.93662±0.00008	0.93752±0.00008	0.93895±0.00005
313	0.93333±0.00007	0.93444±0.00006	0.93613±0.00007	0.93721±0.00009	0.93843±0.00007
318	0.93281±0.00009	0.93391±0.00009	0.93565±0.00005	0.93665±0.00005	0.93804±0.00006
323	0.93222±0.00008	0.93331±0.00009	0.93501±0.00009	0.93613±0.00007	0.93761±0.00009
	CsBr Viscosity η (cp)				
298	0.96102±0.00008	0.96528±0.00002	0.97001±0.00009	0.97413±0.00007	0.97838±0.00002
303	0.95929±0.00001	0.96426±0.00004	0.96885±0.00005	0.97341±0.00009	0.97758±0.00002
308	0.95701±0.00009	0.96352±0.00008	0.96742±0.00008	0.97215±0.00005	0.97629±0.00001
313	0.95643±0.00007	0.96253±0.00007	0.96733±0.00007	0.97186±0.00004	0.97607±0.00003
318	0.95558±0.00002	0.96147±0.00003	0.96703±0.00007	0.97121±0.00009	0.97597±0.00003
323	0.95497±0.00003	0.95859±0.00001	0.96249±0.00001	0.96679±0.00001	0.97055±0.00005

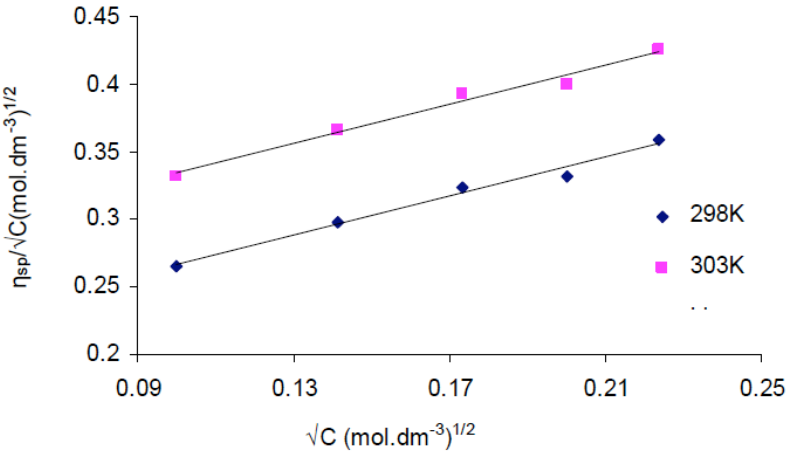

Figure 1: $\frac{\eta_{sp}}{\sqrt{C}}$ vs $\sqrt{C}$ of LiBr in AN at 298K, 303K. (η_{sp} is Specific viscosity, C is molar concentration).

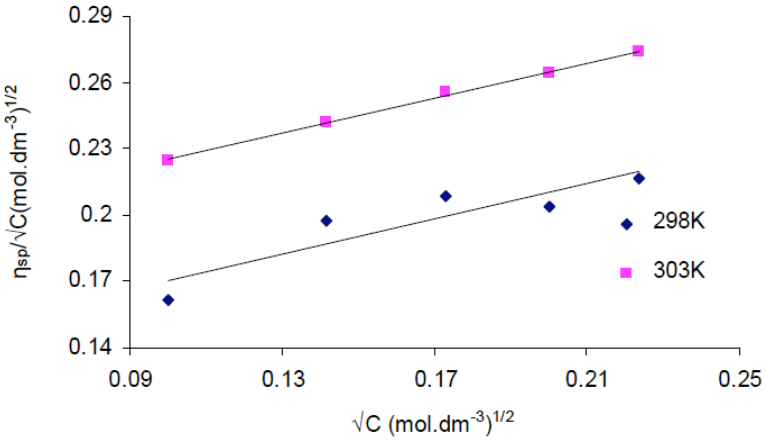

Figure 2: $\frac{\eta_{sp}}{\sqrt{C}}$ vs $\sqrt{C}$ of LiBr in 3-HPN at 298K, 303K.

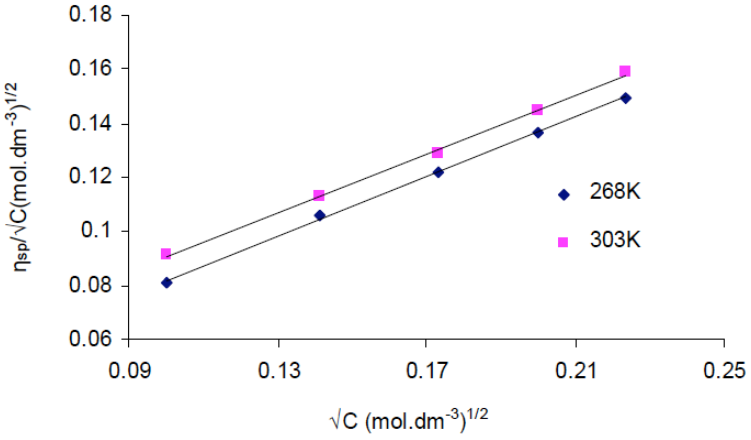

Figure 3: $\frac{\eta_{sp}}{\sqrt{C}}$ vs $\sqrt{C}$ of LiBr in 50 % AN+ 3-HPN at 298K, 303K.

versus $\sqrt{C}$. The represented linear plots of LiBr in AN, 3-HPN and 50% mixture of AN+3-HPN at 298K and 303K are shown in Figures **1**, **2** and **3**. Ion-ion and ion-solvent interactions characterizing the behavior of electrolytes *A* and *B* are the constants at a giving temperatures and characteristic of solutions.

The *A*-coefficient is related to the effect of ion size on the viscosity. The values of *A*-coefficient for all alkali metal bromides in AN, 3-HPN and 50% mixture of AN+3-HPN are tabulated in Tables **5**, **6** and **7** respectively. The values of *A*-coefficient are small and positive there by indicating weak ion-ion columbic interactions. The values of *A*-coefficient are found to increase with the rise of temperature. This may be due to the interpenetration effect (cation-cation) and (cation-anion) which brings ions together [17].

Table 5: Jones Dole *A*-Coefficients of LiBr in AN at Various Temperatures

Temperatures (K)	*A*- Coefficient ($dm^3.mol^{-1}$)^{½}
	LiBr
298	0.1930
303	0.2612
308	0.3386
313	0.3626
318	0.4002
323	0.5382

B-coefficient of viscous flow is depends on ion-solvent interactions and on the relative size of solute and solvent molecule. *B*-coefficient provides information concerning the solvation and their behavior on structure of the solvent in the near environment of the solute molecules. *B*-coefficient reflects the size and shape effect of a solute, structure effect caused by ion-solvent coefficient. Since some activation parameters of viscous flow can be obtained from *B*-coefficient values [18, 19]. The *B*-coefficient of all alkali metal bromides in AN, 3-HPN and 50% mixture of AN+3-HPN are tabulated in Tables **8**, **9** and **10**. The value of the *B*-coefficient is found to be positive and decreases with increasing temperature because electrolytes behave as structure maker in solvents. In ionic solutions of electrolyte interactions arise between ions and solvents, which are effected on the tendency of reactivity of ions. The viscosities of alkali metal bromides in 50% mixture of AN+3-HPN are less than in 3-HPN because the addition of AN causes the breaking of the hydrogen bond between 3-HPN molecules thus leading to a less structured solvent and to a rapid decrease in the viscosity of solvent as well as in bromide salt solutions. This would lead one to expect a decrease in structure breaking ability of ions when the AN had been added [12]. The power of reactivity of an electrolyte which causes the alteration in the solvent structure depends on the ionic strength, charge, size and shape of the electrolyte.

Table 6: Jones Dole *A*-Coefficients of Alkali Metal Bromides in 3-HPN at Various Temperatures

Temperatures (K)	*A*- Coefficient ($dm^3.mol^{-1}$)$^{1/2}$				
	LiBr	NaBr	KBr	RbBr	CsBr
298	0.1320	0.1281	0.1318	0.1328	0.1389
303	0.1857	0.4026	0.1924	0.1903	0.1952
308	0.2373	0.2368	0.2430	0.2369	0.2414
313	0.3034	0.3047	0.3064	0.3004	0.3036
318	0.4034	0.3523	0.3623	0.3450	0.3478
323	0.4258	0.3778	0.3856	0.3925	0.3867

Table 7: Jones Dole *A*-Coefficients of Alkali Metal Bromides in 50% AN+3-HPN at Various Temperatures

Temperatures (K)	*A*- Coefficient ($dm^3.mol^{-1}$)$^{1/2}$				
	LiBr	NaBr	KBr	RbBr	CsBr
298	0.0268	0.0212	0.0173	0.0283	0.0095
303	0.0360	0.0284	0.0309	0.0394	0.0206
308	0.0480	0.0425	0.0397	0.0511	0.0321
313	0.0554	0.0499	0.0463	0.0555	0.4014
318	0.0641	0.0579	0.0539	0.0624	0.0477
323	0.0954	0.0953	0.0768	0.0291	0.0755

Table 8: Jones Dole *B*-Coefficients of LiBr in AN at Various Temperatures

Temperatures (K)	*B*- Coefficient ($dm^3.mol^{-1}$)
298	0.7306
303	0.7290
308	0.7222
313	0.6568
318	0.6467
323	0.4510

The *B*-coefficient of bromide salts in pure AN, 3-HPN and in mixture are positive and decrease with increasing temperature. The decrease in positive values with increasing temperature reveals that electrolytes behave as structure maker in protic and aprotic solvents, it indicates that viscosity decreases due to the solvent structure. Distortion of solvent structure is small which leads to the positive values of *B*-coefficient structure making in nature [20].

The energy of activation ΔE_v, was evaluated from the Arrhenius relation [21, 22] and the representative plots of $\log\eta$ versus $\frac{1}{T}$ as a function of electrolytes concentration shown in Figure **4** in AN of 0.01 $mol.dm^{-3}$ LiBr while Figures **5** and **6** in 3-HPN and50% AN +3-HPN mixture of 0.01 $mol.dm^{-3}$ NaBr respectively.

$$\eta = A\exp\left(\frac{\Delta E_v}{RT}\right) \quad (3)$$

$$\log\eta = \log A + \frac{\Delta E_v}{2.303RT} \quad (4)$$

$$\Delta E_v = 2.303(Slope)(R) \quad (5)$$

where η is viscosity R is the universal gas constant. The results for the energy of activation ΔE_v of bromide salts in AN, 3-HPN and AN +3-HPN are tabulated in Tables **11**, **12** and **13** respectively. The energy of activation ΔE_v can be related to the work needed to form a hole in the liquid. The holes are necessary for a liquid to flow. The results show that ΔE_v value increased with the increase in concentration of salts in AN, 3-HPN and 50% AN+3- HPN. This shows that the value of ΔE_v increases with an increase in concentration of electrolytes cause to hindrance in the mobility of molecules and the increase in the size of solute particles so the energy of activation increases. This is again based on hole theory that holes are necessary for solvents to flow [23, 24]. The larger sized solute particles produce less vacant sites and lead to

Table 9: Jones Dole *B*-Coefficients of Alkali Metal Bromides in 3-HPN at Various Temperatures

Temperatures (K)	*B*- Coefficient ($dm^3.mol^{-1}$)				
	LiBr	NaBr	KBr	RbBr	CsBr
298	0.4200	0.4037	0.3774	0.3542	0.2960
303	0.3969	0.4026	0.368	0.3489	0.2909
308	0.3869	0.356	0.3559	0.3356	0.2842
313	0.3571	0.3544	0.3521	0.3331	0.2832
318	0.1296	0.3514	0.3243	0.3201	0.2730
323	0.0286	0.0052	0.0431	0.0142	0.0345

Table 10: Jones Dole *B*-Coefficients of Alkali Metal Bromides in 50% AN+3-HPN at Various Temperatures

Temperatures (K)	*B*- Coefficient ($dm^3.mol^{-1}$)				
	LiBr	NaBr	KBr	RbBr	CsBr
298	0.5504	0.5731	0.4553	0.4461	0.4269
303	0.5436	0.5662	0.4414	0.4339	0.4192
308	0.5341	0.5552	0.4384	0.4278	0.4088
313	0.5255	0.5487	0.4241	0.4210	0.4014
318	0.5157	0.5402	0.4173	0.4148	0.3934
323	0.2700	0.2819	0.2282	0.2049	0.1730

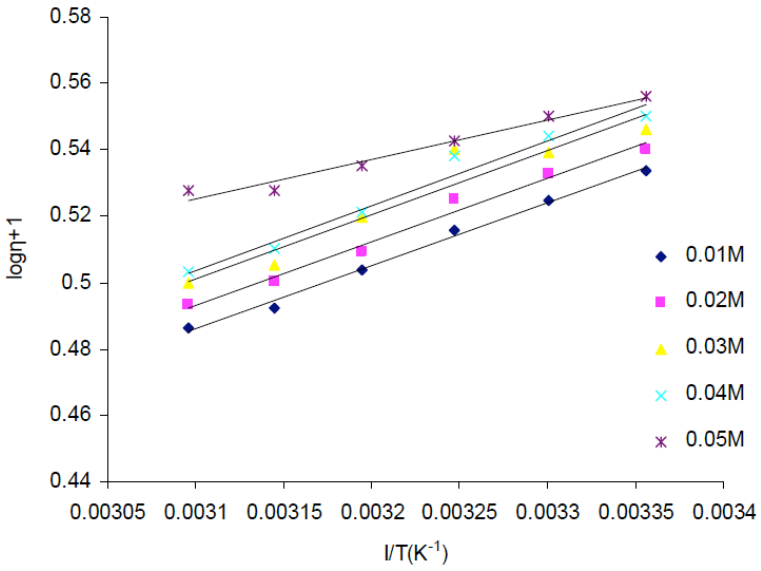

Figure 4: log η vs 1/T of LiBr in AN(η is viscosity T is temperature).

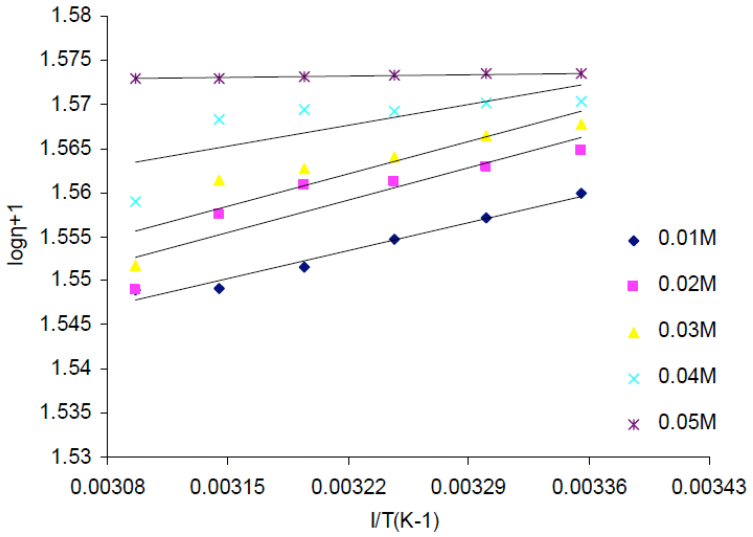

Figure 5: log η vs 1/T of NaBr in 3-HPN.

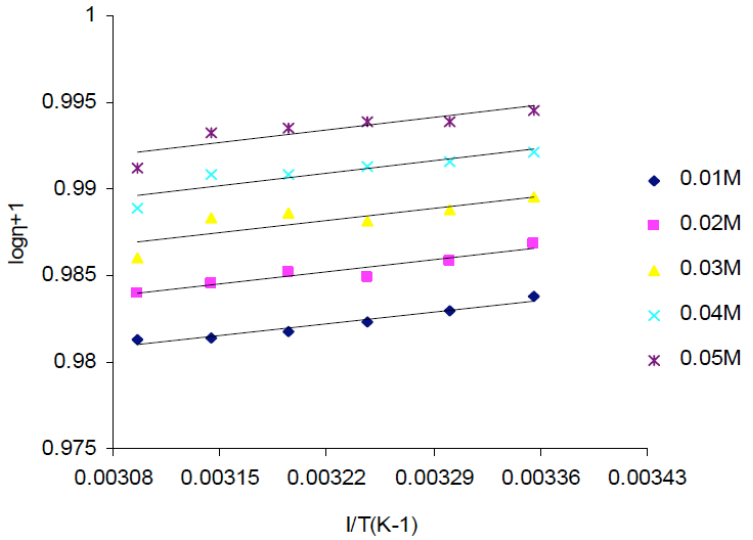

Figure 6: log η vs 1/T of NaBr in 50 % AN + 3-HPN.

an increase in viscosity and large values of energy of activation ΔE_v .

Table 11: Energy of Activation ΔE_V of LiBr in AN

Concentration (mol.dm^{-3})	ΔE_V 10^{-2} (KJ.mol^{-1})
0.01	36.466
0.02	36.556
0.03	37.270
0.04	37.314
0.05	22.768

The energy change of activation ΔG for viscous flow is given by [22]

$$\Delta G = \frac{RT \ln \eta V}{hN_A} \tag{6}$$

where V may be regarded as the volume of one mole of solvent particles, h is Planck's constant,

N_A is Avogadro's number and R is general gas constant.

$$V = \frac{1000}{n_1 + n_2 v} \tag{7}$$

where n_1, n_2 are number of moles of solvent and solute respectively while v represent the number of species are present in solution in dissociation form.

$$n_1 = \frac{1000d - M_2 n_2}{M_1} \tag{8}$$

where d is density of solvent, M_1, M_2 are molecular masses of solvent and solute respectively for solvent mixture 50% AN+3-HPN averaged molecular mass M_{av} was used to calculate the molar volume of AN+3-HPN mixture.

$$V = \frac{M_{av}}{d} \tag{9}$$

$$M_{av} = \frac{M_1 M_2}{x_1 M_1 + x_2 M_2} \tag{10}$$

where x_1, x_2 are The mol fraction of AN and 3-HPN respectively M_1, M_2 show molecular mass of AN and 3-HPN.

The values of energy change of activation ΔG are tabulated in Table **14** of LiBr in AN, **15** and **16** for alkali metal bromides in 3-HPN and 50% AN+3-HPN respectively. The results show that the value of Gibbs energy change of activation ΔG increases with the increase in concentration of salts and temperature. The positive values of Gibbs energy change of activation increase with the increase in concentration of electrolytes and also with the rise of temperature indicate the association of electrolytes molecules with AN, 3-HPN and 50% AN+ 3- HPN mixture. The Gibbs energy change of activation controls the rate of flow in fluid which is governed by the ability of molecules to

Table 12: Energy of Activation ΔE_V of Alkali Metal Bromides in 3-HPN

Concentration (mol.dm^{-3})	ΔE_V 10^{-2} (KJ.mol^{-1})				
	LiBr	NaBr	KBr	RbBr	CsBr
0.01	7.664	8.614	8.193	8.922	8.960
0.02	7.686	9.973	8.826	8.959	9.088
0.03	7.844	9.989	8.841	8.988	9.292
0.04	1.845	6.496	5.451	4.891	4.146
0.05	0.430	0.398	0.391	0.952	0.936

Table 13: Energy of Activation ΔE_V of Alkali Metal Bromides in 50% AN+ 3-HPN Mixture

Concentration (mol.dm^{-3})	ΔE_V 10^{-2} (KJ.mol^{-1})				
	LiBr	NaBr	KBr	RbBr	CsBr
0.01	1.988	1.879	2.167	2.292	2.015
0.02	2.092	1.907	2.167	2.107	2.024
0.03	2.112	1.919	2.195	2.117	2.029
0.04	2.141	1.965	2.207	2.127	2.037
0.05	2.1967	1.982	2.218	2.133	2.055

Table 14: Energy Change of Activation ΔG of LiBr in AN at Various Temperatures

Temperature K	ΔG 10^{-3} (KJ.mol^{-1})				
	0.01	0.02	0.03	0.04	0.05
	Concentration(mol.dm^{-3}) of LiBr				
298	60.802	60.837	60.867	60.885	60.917
303	61.775	61.802	61.843	61.880	61.902
308	62.758	62.790	62.832	62.866	62.891
313	63.710	63.736	63.792	63.791	63.875
318	64.681	64.721	64.744	64.766	64.862
323	65.690	65.727	65.759	65.759	65.908

Table 15: Energy Change of Activation ΔG of Alkali Metal Bromides in 3-HPN at Various Temperatures

Temperature K	ΔG 10^{-3} (KJ.mol^{-1})				
	Concentration(mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	LiBr				
298	67.294	67.318	67.330	67.342	67.357
303	68.409	68.434	68.455	68.473	68.488
308	69.524	69.558	69.572	69.605	69.619
313	70.636	70.682	70.694	70.736	70.751
318	71.757	71.805	71.823	71.866	71.882
323	72.886	72.896	72.916	72.982	73.012
NaBr					
298	67.292	67.318	67.332	67.344	67.358
303	68.407	68.437	68.455	68.475	68.490
308	69.523	69.558	69.572	69.606	69.621
313	70.632	70.686	70.695	70.736	70.751
318	71.748	71.796	71.818	71.856	71.882
323	72.876	72.874	72.888	72.930	73.013
KBr					
298	67.289	67.312	67.331	67.345	67.358
303	68.402	68.434	68.455	68.475	68.489
308	69.518	69.558	69.576	69.606	69.620
313	70.628	70.682	70.695	70.736	70.751
318	71.744	71.797	71.818	71.867	71.881
323	72.877	72.880	72.902	72.939	73.012
RbBr					
298	67.295	67.317	67.330	67.342	67.356
303	68.409	68.436	68.453	68.472	68.486
308	69.525	69.556	69.569	69.602	69.616
313	70.636	70.678	70.693	70.730	70.745
318	71.751	71.786	71.816	71.848	71.876
323	72.876	72.891	72.898	72.950	73.004

(Table 15). Continued.

Temperature K	$\Delta G\ 10^{-3}$ (KJ.mol^{-1})				
	Concentration(mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	CsBr				
298	67.290	67.319	67.332	67.345	67.352
303	68.404	68.437	68.455	68.476	68.481
308	69.521	69.558	69.572	69.606	69.612
313	70.631	70.679	70.695	70.734	70.740
318	71.746	71.788	71.819	71.851	71.871
323	72.871	72.892	72.897	72.963	73.000

Table 16: Energy Change of Activation ΔG of Alkali Metal Bromides in 50% AN+3- HPN Mixture at Various Temperatures

Temperature K	$\Delta G\ 10^{-3}$ (KJ.mol^{-1})				
	Concentration(mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	LiBr				
298	63.657	63.673	63.687	63.701	63.715
303	64.752	64.741	64.756	64.772	64.787
308	65.791	65.808	65.824	65.842	65.856
313	66.865	66.885	66.905	66.918	66.933
318	67.942	67.964	67.983	66.998	68.011
323	69.020	69.033	69.045	69.063	69.079
	NaBr				
298	63.655	63.672	63.686	63.700	63.713
303	64.723	64.739	64.755	64.770	64.783
308	65.791	65.804	65.823	65.840	65.855
313	66.864	66.884	66.904	66.916	66.932
318	67.941	67.960	67.982	67.997	68.010
323	69.019	69.034	69.046	69.063	69.077
	KBr				
298	63.652	63.694	63.673	63.688	63.970
303	64.720	64.768	64.746	64.758	64.769
308	65.784	65.838	65.814	65.826	65.835
313	66.860	66.907	66.888	66.905	66.914
318	67.937	67.976	67.967	67.982	67.994
323	69.013	69.041	69.034	69.049	69.058
	RbBr				
298	63.670	63.680	63.688	63.700	63.708
303	64.734	64.748	64.755	64.766	64.776
308	65.799	65.814	65.824	65.833	65.844
313	66.866	66.882	66.889	66.902	66.912
318	67.933	67.949	67.958	67.970	67.982
323	69.001	69.012	69.020	69.030	69.038

(Table 16). Continued.

Temperature K	ΔG 10^{-3} (KJ.mol^{-1})				
	Concentration(mol.dm^{-3})				
	0.01	0.02	0.03	0.04	0.05
	CsBr				
298	63.678	63.686	63.694	63.702	63.709
303	64.744	64.754	64.761	64.770	64.778
308	65.808	65.821	65.828	65.838	65.845
313	66.876	66.889	66.897	66.906	66.914
318	67.943	67.956	67.966	67.975	67.984
323	69.011	69.018	69.024	69.033	69.039

move in to the prepared hole and the readiness with which the liquid produces the hole [17]. The results showed that the values of ΔG increase with increase in temperature due to increase in salt-solvent interaction.

The change in entropy of activation ΔS is given by [27].

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{11}$$

The energy of ΔE_v does not differ appreciably from activation enthalpy (Δ*H*).

$$\Delta E_v = \Delta H \tag{12}$$

$$\Delta S = \frac{\Delta E_v - \Delta G}{T} \tag{13}$$

The results of entropy change of activation ΔS of LiBr in AN and LiBr, NaBr, KBr, RbBr and CsBr in 3-HPN and 50% AN+3-HPN at different temperatures are summarized in Tables **17**, **18** and **19** respectively. The entropy of solution at all temperatures is found negative and increases with increasing the concentration of electrolytes and also with increase in temperature with some variations indicate more order in the system. The negative values of entropy change of activation ΔS shows that the species are formed at activated state are more ordered than the initial state [26].

The excess molar volume V_m^E has been calculated by the following equation.

$$V_m^E = \left[\frac{x_1 M_1 + x_2 M_2}{d} - \left\{ \frac{x_1 M_1}{d_1} + \frac{x_2 M_2}{d_2} \right\} \right] \tag{14}$$

where x_1, M_1, d_1 are mole fraction, molecular mass and density respectively of AN x_2, M_2, d_2 are corresponding properties of 3-HPN and d is the density of solution.

The values of V_m^E are reported in Table **20**. The V_m^E values are found to be negative at different temperatures. The negative values increases as the temperature increases. The negative values shows existence of specific interactions between the mixing components [27]. The negative V_m^E represent that the factor responsible for concentration of volume on

Table 17: Entropy Change of Activation ΔS of LiBr in AN at Various Temperatures

Temperature (K)	ΔS 10^{-2} (J.K $^{-1}$.mol^{-1})				
	0.01	0.02	0.03	0.04	0.05
	LiBr				
298	-1.918	-1.919	-1.917	-1.918	-1.968
303	-1.918	-1.919	-1.918	-1.919	-1.968
308	-1.919	-1.920	-1.911	-1.920	-1.968
313	-1.919	-1.920	-1.919	-1.919	-1.968
318	-1.919	-1.920	-1.919	-1.919	-1.968
323	-1.921	-1.922	-1.920	-1.920	-1.970

Table 18: Entropy Change of Activation ΔS of Alkali Metal Bromides in 3-HPN at Various Temperatures

Temperature (K)	$\Delta S\ 10^{-2}$ (J.K $^{-1}$.mol^{-1})				
	0.01	0.02	0.03	0.04	0.05
	LiBr				
298	-2.229	-2.226	-2.226	-2.238	-2.259
303	-2.229	-2.226	-2.226	-2.238	-2.259
308	-2.229	-2.226	-2.226	-2.239	-2.259
313	-2.229	-2.226	-2.227	-2.239	-2.259
318	-2.229	-2.226	-2.227	-2.239	-2.259
323	-2.230	-2.225	-2.226	-2.238	-2.259
NaBr					
298	-2.229	-2.226	-2.226	-2.238	-2.259
303	-2.229	-2.226	-2.226	-2.238	-2.259
308	-2.229	-2.226	-2.226	-2.239	-2.259
313	-2.229	-2.226	-2.227	-2.239	-2.259
318	-2.229	-2.226	-2.227	-2.239	-2.259
323	-2.230	-2.225	-2.226	-2.238	-2.259
KBr					
298	-2.229	-2.226	-2.226	-2.238	-2.259
303	-2.229	-2.226	-2.226	-2.238	-2.259
308	-2.229	-2.226	-2.226	-2.239	-2.259
313	-2.229	-2.226	-2.227	-2.239	-2.259
318	-2.229	-2.226	-2.227	-2.239	-2.259
323	-2.230	-2.225	-2.226	-2.238	-2.259
RbBr					
298	-2.228	-2.229	-2.229	-2.243	-2.257
303	-2.228	-2.229	-2.230	-2.24	-2.257
308	-2.228	-2.229	-2.230	-2.244	-2.257
313	-2.228	-2.229	-2.230	-2.244	-2.257
318	-2.228	-2.229	-2.230	-2.243	-2.257
323	-2.229	-2.229	-2.229	-2.243	-2.257
CsBr					
298	-2.228	-2.228	-2.228	-2.246	-2.257
303	-2.228	-2.229	-2.228	-2.246	-2.257
308	-2.228	-2.229	-2.229	-2.246	-2.257
313	-2.228	-2.229	-2.229	-2.247	-2.257
318	-2.228	-2.229	-2.229	-2.246	-2.257
323	-2.228	-2.228	-2.228	-2.246	-2.257

Table 19: Entropy Change of Activation ΔS of Alkali Metal Bromides in 50% AN+ 3-HPN Mixture at Various Temperatures

Temperature (K)	ΔS 10^{-2} (J.K $^{-1}$.mol^{-1})				
	0.01	0.02	0.03	0.04	0.05
	LiBr				
298	-2.129	-2.130	-2.130	-2.310	-2.131
303	-2.130	-2.130	-2.130	-2.131	-2.131
308	-2.130	-2.123	-2.130	-2.131	-2.131
313	-2.123	-2.130	-2.131	-2.031	-2.131
318	-2.130	-2.131	-2.131	-2.132	-2.132
323	-2.131	-2.131	-2.131	-2.132	-2.132
NaBr					
298	-2.130	-2.130	-2.131	-2131	-2.131
303	-2.130	-2.130	-2.131	-2.131	-2.132
308	-2.130	-2.130	-2.131	-2.131	-2.132
313	-2.130	-2.131	-2.131	-2.132	-2.132
318	-2.131	-2.131	-2.132	-2.132	-2.132
323	-2.131	-2.131	-2.132	-2.132	-2.132
KBr					
298	-2.129	-2.130	-2.129	-2.130	-2.130
303	-2.129	-2.130	-2.130	-2.1230	-2.130
308	-2.129	-2.130	-2.130	-2.130	-2.130
313	-2.129	-2.131	-2.130	-2.130	-2.131
318	-2.130	-2.131	-2.130	-2.131	-2.131
323	-2.123	-2.131	-2.130	-2.131	-2.131
RbBr					
298	-2.130	-2.130	-2.130	-2.131	-2.131
303	-2.130	-2.130	-2.131	-2.131	-2.131
308	-2.130	-2.130	-2.131	-2.131	-2.131
313	-2.130	-2.130	-2.131	-2.131	-2.131
318	-2.130	-2.131	-2.131	-2.131	-2.131
323	-2.130	-2.130	-2.131	-2.131	-2.131
CsBr					
298	-2.232	-2.233	-2.233	-2.254	-2.259
303	-2.232	-2.233	-2.233	-2.254	-2.259
308	-2.232	-2.233	-2.234	-2.254	-2.259
313	-2.232	-2.234	-2.234	-2.254	-2.259
318	-2.232	-2.234	-2.234	-2.254	-2.259
323	-2.233	-2.233	-2.233	-2.254	-2.259

mixing of the components. The negative V_m^E indicates the presence of strong molecular interactions between the components of mixture. The optimum condition is directly related to the difference in molecular size and intermolecular interactions between unlike molecules creating associated complexes as well as being effected by the breaking the interactions between same molecules [28, 29].

Table 20: Excess Molar Volume V_m^E of 50% AN+3-HPN Mixture at Various Temperatures

Temperatures (K)	V_m^E (cm^3.mol^{-1})
298	-2.877
303	-3.137
308	-3.169
313	-3.295
318	-3.308
323	-3.460

CONCLUSION

Activation and thermodynamic parameters such as $\Delta E_v, \Delta G$ and ΔS were evaluated by using the density and viscosity data of electrolytes (i.e. alkali metal bromides).

The effect of temperature and concentration of electrolytes were observed on the basis of ion-solvent interactions. The positive decreasing order in *B*-coefficient with increasing the temperature suggests that alkali metal bromides behave as structure maker in solvents. The ΔE_v increases with increase in concentration of electrolytes cause to hindrance in the mobility of molecules. ΔG values of electrolytes in AN and 50% AN +3-HPN mixture linearly increases of electrolytes with increase in temperature and concentration. This increase is due to the association of electrolytes molecules with solvent mixture. Negative values of ΔS show more order in viscous flow system. While negative V_m^E values indicate strong molecular interaction between components of mixture.

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