Asian Journal of Chemistry Vol. 5, No. 3 (1993), 632–636

The Evaluation of Thermodynamic Parameters of Viscous Flow in Dimethylformamide (DMF)-Water Mixtures for Chlorides and Bromides of Calcium, Strontium and Barium at 25° and 35°C

S.C. SINHA*, P.C. SINHA† and D. PRASAD‡
Department of Chemistry, J.R.S. College
Jamalpur-811 214, India

The thermodynamic parameters for viscous flow, viz., ΔE*, ΔF* and ΔS* at 25° and 35°C have been calculated for the chlorides and bromides of calcium, strontium and barium in DMF-water mixtures of various composition using the method of Nightingale and Benck's equation based on the application of Eyring's theory of absolute reaction rate. The activation parameters for viscous flow have been obtained to throw light on the mechanism of viscous flow. The values for ΔE* and ΔF* increase with the solvent composition and decrease with the rise of temperature for all electrolyte solutions. Barium halides cause a larger decrease in ΔE* of solvent system than the corresponding halides of strontium and calcium at all solvent composition as well as on both the temperatures. ΔS* value decreases with solvent composition as well as with the rise of temperature for all the electrolyte solutions. In the case of solvent, ΔS* reaches a maximum in the vicinity of 20% DMF-water mixture at both the temperatures, suggesting that the solvent has the highest degree of structure near this composition.

INTRODUCTION

A large number of data are available in literature on the applicability of Jone-Dole equation[1] for electrolyte solutions in both aqueous and mixed solvents as already mentioned in our previous paper[2]. The work on the viscosity measurement of potassium iodide, tetraethyl ammonium bromide, LiCl, $LiNO_3$ and $MClO_4$ (M=Li, Na, K) in DMF-water mixture at different compositions and at various temperatures has been reported earlier[3, 4]. Domench and Costa[4] have applied transition-state treatment for calculation of the contribution per mole of the solute to the free energy of activation for viscous flow for certain electrolytes at 25°, 30° and 35°C while Nightingale and Benck[5] have utilised the data to interpret the ion-solvent interaction at 25°C in aqueous solution of several

---

†Department of Chemistry, B.N. College, Patna-800 004, India.

‡P.G. Department of Chemistry, University of Bihar, Muzaffarpur-842 001, India.

electrolytes by calculating thermodynamic parameter ΔE*, ΔF* and ΔS* for viscous flow with the help of Erying's method based on the theory of absolute reaction rate to the phenomena of viscous flow. The present investigation reports the evaluation of these thermodynamic parameters for viscous flow of chlorides and bromides of calcium, strontium and barium at 25° and 35°C using the method of Nightingale and Benck[5] in order to study the ion-solvent interaction and also to throw light on the mechanism of viscous flow in DMF-water mixed solvent.

EXPERIMENTAL

The experimental technique for the purification of salts used, together with the preparation of $CaCl_2$, were the same as previously reported[2]. The experimental procedure for the preparation of DMF (Reidal), preparation of solvent and solutions, measurement of viscosity and density of solvent and solutions were also the same as previously reported[2].

Methods for the basis of calculation and obtaining results have been described as previously reported[2]. The maximum fluctuation in temperature was ± 0.1°C while the average deviation in viscosity measurement was less than 0.1%. The accuracy in ΔE* measurement was ±0.04 kcals.

The values obtained for ΔE*, ΔF* and ΔS* for the electrolytes under investigation at 25° and 35°C are recorded in Tables 1 and 2 respectively.

TABLE 1
VALUES OF THERMODYNAMIC PARAMETERS FOR VISCOUS FLOW OF SOLUTES AT 25°C

Solutes	ΔE* (Kcals) ± 0.04				ΔF* (Kcals)				ΔS* (e.u.)			
	Solvent composition (wt % of DMF)				Solvent composition (wt % of DMF)				Solvent composition (wt % of DMF)			
	0	10	20	40	0	10	20	40	0	10	20	40
Solvent	4.01	4.445	4.743	5.066	2.19	2.367	2.542	2.886	6.1	6.973	7.385	7.315
$CaCl_2$		3.840	3.905	4.058		2.579	2.764	3.140		4.230	3.827	3.080
$SrCl_2$		3.516	3.582	3.732		2.581	2.765	3.143		3.137	2.739	1.976
$BaCl_2$	3.10	3.193	3.260	3.405	2.30	2.522	2.707	3.086	2.7	2.250	1.855	1.070
$CaBr_2$		3.893	3.989	4.139		2.589	2.807	3.148		4.375	3.966	3.324
$SrBr_2$		3.601	3.661	3.807		2.591	2.771	3.153		3.388	2.985	2.194
$BaBr_2$		3.273	3.335	3.478		2.529	2.714	3.097		2.496	2.082	1.277

TABLE 2
VALUES OF THERMODYNAMIC PARAMETERS FOR VISCOUS FLOW OF SOLUTES AT 35°C

Solute	ΔE^* (Kcals) ± 0.04			ΔF^* (Kcals)			ΔS^* (e.u.)		
	Solvent composition (wt % of DMF)			Solvent composition (wt % of DMF)			Solvent composition (wt % of DMF)		
	10	20	40	10	20	40	10	20	40
Solvent	4.205	4.651	4.869	2.306	2.478	2.812	6.165	7.055	6.678
$CaCl_2$	3.715	3.813	3.948	2.548	2.735	3.108	3.788	3.501	2.725
$SrCl_2$	3.388	3.486	3.621	2.557	2.744	3.117	2.697	2.408	1.636
$BaCl_2$	3.066	3.167	3.299	2.506	2.695	3.077	1.816	1.532	0.720
$CaBr_2$	3.801	3.892	4.025	2.552	2.738	3.114	4.054	3.746	2.958
$SrBr_2$	3.469	3.560	3.692	2.556	2.747	3.124	2.930	2.639	1.844
$BaBr_2$	3.142	3.238	3.366	2.514	2.704	3.081	2.093	1.734	0.925

RESULTS AND DISCUSSION

The results of the study revealed that the mole-fraction of DMF upto 0.15 in DMF-water mixture, ΔE^* values are always found to be positive with the increases in the mole fraction of DMF in the solvent. The values for ΔE^* decrease with increase in temperature as the value at 35°C (Table 2) are smaller than the corresponding values at 25°C (Table 1). ΔE^* value for the solvent increases with the increase in mole-fraction of DMF. This may be due to a phenomenon of hydration in which hydrogen bonds present in water molecule are broken and a bulkier three-dimensional DMF-water mixed species are formed in the system which are bulkier than either of the pure solvents. This results in the mixed solvent being more viscous. These facts with the increasing mole-fraction in the system have also been observed from the nature of curve obtained by plotting $\ln \eta$ vs. $1/T$. The process of hydration of DMF is exothermic and, therefore, an increase in the temperature of the system decreases the extent of hydration due to thermal agitation in solution resulting in a decrease in concentration of three-dimensional DMF-water mixed molecule in the system. Thus, the system is less viscous at 35°C than at 25°C which results in a decrease in ΔE^* value at higher temperature.

The addition of electrolytes in the system is always accompanied by a decrease in ΔE^* values for all percentage (%) composition of mixed solvent. This is due to the breaking of bond of bulkier DMF-water molecule present in the system. The system has lesser number of bulkier DMF-water molecules leading to a gradual decrease in viscosity. Chloride and bromide of barium cause a larger decrease in ΔE^* for the solvent in comparison to the chloride and bromide of strontium and calcium at the given solvent composition at both the temperatures. This indicates that the bond breaking of the system by ions is according to the order: $Ba^{++} > Sr^{++} > Ca^{++}$. This is due to larger crystal radii of Ba^{++}

It is also evident from the data for ΔE^*, chlorides always decrease the ΔE^*

tendency of smaller Cl^- ion for breaking the bond of bulkier DMF-water mixed solvent than Br^- ion.

The differences in ΔE^* values for different electrolytes under investigation are found to be almost constant and the following relationship is observed at all compositions of solvent on both temperatures. (Table 3).

$$(\Delta E_{CaX_2} - \Delta E_{BaX_2}) = \{(\Delta E_{CaX_2} - \Delta E_{SrX_2}) + (\Delta E_{SrX_2} - \Delta E_{BaX_2})\}$$

TABLE 3: VALUES OF DIFFERENCE IN ΔE^* (kcals) OF SOLUTES AT 25°C and 35°C.

Temperature	25°C			35°C		
Solutes	Solvent Composition (wt % of DMF)			Solvent Composition (wt % of DMF)		
	10	20	40	10	20	40
$\Delta E_{CaCl_2} - \Delta E_{SrCl_2}$	0.324	0.323	0.326	0.327	0.327	0.327
$\Delta E_{SrCl_2} - \Delta E_{BaCl_2}$	0.323	0.322	0.327	0.322	0.319	0.322
$\Delta E_{CaCl_2} - \Delta E_{BaCl_2}$	0.647	0.645	0.653	0.649	0.646	0.649
$\Delta E_{CaBr_2} - \Delta E_{SrBr_2}$	0.292	0.328	0.331	0.332	0.332	0.333
$\Delta E_{SrBr_2} - \Delta E_{BaBr_2}$	0.328	0.326	0.329	0.327	0.322	0.326
$\Delta E_{CaBr_2} - \Delta E_{BaBr_2}$	0.620	0.654	0.661	0.659	0.654	0.659

This is probably due to additive character of ΔE^*, and these results also suggest that cations have a definite effect on breaking of bond of solvent structure of the system and the phenomena is related to ths size and charge of ions. The addition of ions like Ba^{2+}, Sr^{2+} and Ca^{2+} favours the flow process by changing the solvent composition.

The values for ΔF^* for electrolytes (Tables 1 and 2) are approximately constant and have slightly higher value than corresponding values at 25°C in water both in cases of solvent and solutions. The increase in ΔF^* value with the mole-fraction of DMF in the solvent at 25° and 35°C as well as the decrease in ΔF^* value with the increase in temperature also supports bond breaking phenomena in the solvent structure by the presence of electrolytes.

Form the data for ΔS^* (Tables 1 and 2), it is evident that they have positive value having similar trends to those of ΔE^*. This also denotes that the formation of the transition state is associated with bond breaking and a decrease in order of solvent structure. In case of solvent, ΔS_0^* value reaches a maximum in the vicinity of 20% DMF-water mixture on both the temperatures. Therefore, it may be assumed that the solvent has the highest degree of structure of solvent in 20% DMF-water mixture as previously reported[2].

The curves representing the variation of ΔE^* with mole-fraction of DMF in the solvent at 25°C are shown in Fig. 1. The values for 0% DMF i.e. for pure water obtained at 25°C are in close agreement with the values reported by Nightingale and Benck[5].

ACKNOWLEDGEMENTS

One of the authors (SCS) thanks the UGC, New Delhi for the award of the Junior Research Fellowship and Prof. T. Sharma, Head of the Department of Chemistry, University of Bihar, Muzaffarpur for providing laboratory facilities.

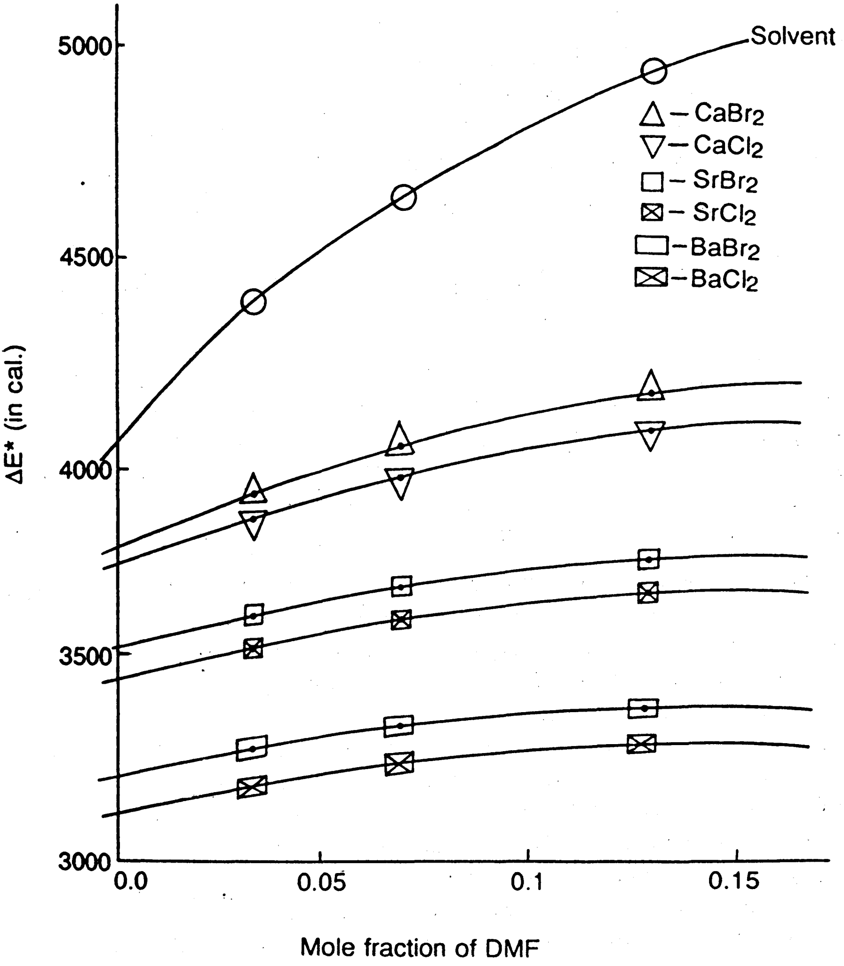

Fig. 1 ΔE* as a function of mole fraction of DMF in 10% DMF water mixture at 25°C

REFERENCES

1. G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).
2. D. Prasad, P.C. Sinha and S.C. Sinha, *Asian J. Chem.*, **4**, 696 (1992).
3. P.K. Tikoo and Raj Deo Singh, *Electrochim. Acta*, **26**, 1057 (1981).
4. J. Domenech and J.M. Costa, *Electochim, Acta*, **27**, 1789 (1982); 28, 1789 (1983).
5. E.R. Nightingale (Jr.) and R.F. Benck, *J. Phys. Chem.*, **63**, 1777 (1959).

(*Received*: 31 December 1991; *Accepted*: 15 October 1992) AJC–498