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Solvation Behaviour of Ions in N,N′-Dimethyl Formamide-Water Mixtures Between 298 and 313 K from Thermodynamic Parameters of Viscous Flow

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Viscosity B-coefficients of Jones-Dole equation for the halides of potassium in dimethyl formamide-water mixtures have been utilised to evaluate the thermodynamic parameters of viscous flow between the temperature range 298 and 313 K, using the method of Nightingale and Benck. Ionic Viscosity B-coefficient as well as ionic thermodynamic parameters of viscous flow are obtained on the basis of the concept that the influence of potassium ion upon the viscous flow phenomenon in DMF-H_2O mixtures is approximately equal to that for chloride ion. These ionic data together with their variation with temperature and mole-fraction of DMF in solvent are utilised in understanding qualitatively the ion-solvent interaction. ΔE^* ion and ΔS^* ion values are found to decrease with temperature as well as mole-fraction of DMF in solvent for halides and monovalent Na^+ ion and K^+ ion. In case of divalent Ca^{2+}, Sr^{2+} and Ba^{2+} ions, ΔS^* ions are found to increase with rise of temperature. Ionic activation energy and ionic activation entropy of viscous flow at studied temperatures decreases in the order of $Na^+ > K^+ > Ca^{2+} > Sr^{2+} > Ba^{2+}$ for cations and $I^- > Br^- > Cl^-$ for anions.

INTRODUCTION

The viscous flow is interpreted as an activated rate process[1] and Nightingale and Benck[2, 3] have utilised the concept in calculating the thermodynamic parameters of viscous flow for a number of electrolytes and ions in aqueous solution at 298 K. The thermodynamic parameters of viscous flow of electrolytes and ions in pure solvent together with mixed solvent have been reported[4–8]. In our previous paper[9–11], we have already reported the thermodynamic parameters of viscous flow for the halides of sodium, calcium, strontium and barium in DMF-H_2O mixture between temperatures 298 and 313 K. In continuation of earlier works, the present investigation reports the evaluation of the thermodynamic parameters for the chloride, bromide and iodide of potassium between the same temperature range and in same solvent compositions. Ionic thermodynamic parameters of viscous flow and ionic viscosity B-coefficient are also obtained from earlier reported data[11]. The data and their variation with temperature and mole-fraction

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of DMF in solvent are critically examined in the light of ion-solvent interaction in mixed solvent system.

EXPERIMENTAL

All the salts used were of AnalaR grade (B.D.H.). Potassium chloride was purified by bubbling chlorine gas through its saturated solution. The resulting solution was crystallised to get bromide and iodide free crystals[12]. The crystals were recrystallised three times with conductance water and tested by the method of Pinching and Bates[13]. The salt was further dried at 393 K for 24 h in electrically heated air-oven. Potassium bromide was recrystallised from counductance water whereas potassium iodide was recrystallised from ethanolic conductance water[14]. These salts were dried at 343 K for 12 h. All the salts were stored in a desiccator over P_2O_5. The experimental procedure for purification of DMF, preparation of solvent and solutions, measurement of viscosity and density of solvent and solution were same as reported earlier[9]. The ranges of concentration were 0.0005 to 0.1 M.

RESULTS AND DISCUSSION

The method for the basis of evaluation of thermodynamic parameters for electrolytes from viscosity B-coefficient have already been described in our earlier papers[9, 11]. The values[15] of parameters A and B of Jone-Dole equation 24 have been utilised in calculation and the calculated values for ΔE^*, ΔF^* and ΔS^* for electrolytes under investigation between temperature ranges 298 and 313 K are recorded in Table-1.

The effect of electrolytes on the thermodynamic parameters of viscous flow cannot be generalised because they are usually associated with the contributions of both cation and anion. Therefore, for general discussion, it is important to consider the role of individual ions, rather than that of salt itself on influencing ion-solvation in mixed solvent. For this purpose the fact that thermodynamic coefficients for ionic solvation are made up of additive ionic contibutions has been utilised. The additive nature of ΔE^* has already been suggested in DMF-H_2O mixtures in our earlier paper[9].

The calculation of ionic parameters of viscous flow has been done assuming that the difference between the activation parameters of solution and the solvent is equal to the sum of the activation parameter for the ionic components and the influence of potassium ion upon the activation parameters of viscous flow in solution is approximately equal to that for chloride ion. The assumption is based on the concept of Nightingale and Benck[2] who have calculated ionic parameters for a number of ions in aqueous solution at 298 K. Thus

$$\Delta E^* - \Delta E_0^* = V_+\Delta E_+^* + V_-\cdot\Delta E^*$$

where ΔE_+^* and ΔE_-^* are the cation and anion activation energies and V_+ and V_- are the numbers of cations and anions respectively, per molecule of salt, ΔE^* and ΔE_0^* are the activation energies of viscous flow for solution and pure solvent respectively.

TABLE-1
THERMODYNAMIC PARAMETERS OF VISCOUS FLOW FOR SOLVENT AND SOLUTE BETWEEN 298 AND 313 K (C = 1 mole/L)

Solvent/ Solute	ΔE^* (Kcal) ±0.04 Solvent composition (Wt % of DMF)				ΔF^* (Kcal) Solvent composition (Wt % of DMF)				ΔS^* (e.u.) Solvent composition (Wt % of DMF)			
	0	10	20	40	0	10	20	40	0	10	20	40
					Temperature 298 K							
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
KCl	3.56	4.430	4.720	5.019	2.18	2.389	2.568	2.959	4.6	6.849	7.221	6.913
KBr		4.433	4.727	5.036		2.388	2.567	2.948		6.862	7.248	7.007
KI		4.436	4.729	5.044		2.387	2.565	2.941		6.876	7.261	7.057
					Temperature 303 K							
Solvent		4.346	4.693	4.965		2.336	2.508	2.848		6.633	7.207	6.987
KCl		4.327	4.665	4.906		2.358	2.534	2.921		6.498	7.033	6.551
KBr		4.330	4.672	4.920		2.357	2.533	2.911		6.511	7.060	6.630
KI		4.333	4.674	4.931		2.356	2.531	2.905		6.525	7.072	6.686
					Temperature 308 K							
Solvent		4.250	4.651	4.869		2.306	2.478	2.812		6.312	7.055	6.678
KCl		4.228	4.621	4.798		2.329	2.505	2.888		6.166	6.871	6.202
KBr		4.231	4.627	4.808		2.328	2.503	2.877		6.179	6.896	6.269
KI		4.234	4.629	4.822		2.327	2.501	2.872		6.192	6.909	6.331
					Temperature 313 K							
Solvent		4.153	4.610	4.776		2.278	2.450	2.786		5.990	6.901	6.358
KCl		4.127	4.577	4.693		2.301	2.477	2.862		5.834	6.709	5.850
KBr		4.130	4.583	4.699		2.300	2.476	2.852		5.847	6.732	5.901
KI		4.134	4.585	4.719		2.299	2.474	2.851		5.863	6.745	5.968

It must be noted here that ΔE_+^* and ΔE_-^* are the change of activation energies of solvent caused by the cation and the anion. ΔE_+^* and ΔE_-^* will hereafter be termed ionic activation energies, but should not be confused with the activation energies for ions. By these definitions, ionic activation energies are interpreted as the change in activation energy for the movement of solvent molecules due to the presence of ions. The activation energy for an ion is that activation energy for an ion itself to make a "jump" into a neighbouring "hole". The latter is assumed to make a negligible contribution to the total observed activation energy at low concentration for this model. Similarly,

$$\Delta S^* - \Delta S_0^* = V_+\Delta S_+^* + V_-\Delta S_-^*$$

where ΔS_+^* and ΔS_-^* are ionic entropy for viscous flow and ΔS^* and ΔS_0^* are the entropies of activation for viscous flow of solution and solvent respectively. The values of ionic energy and ionic entropy of activation of viscous flow for ions in DMF-H_2O mixtures between the temperature range 298 and 313 K at concentration 1 M are recorded in Table-2.

TABLE-2
IONIC THERMODYNAMIC PARAMETERS OF VISCOUS FLOW BETWEEN 298 AND 313 K (C = 1 MOLE/LITRE)

Ion	Temperature K	$\Delta E^{*}_{\pm ion}$ (Cal) Solvent composition (wt % of DMF)				$\Delta S^{*}_{\pm ion}$ (e.u.) Solvent composition (wt % of DMF)			
		0%[2]	10%	20%	40%	0%[2]	10%	20%	40%
K^+	298	–220	–7.750	–11.500	–23.500	–0.75	–0.062	–0.082	–0.201
	303		–9.500	–13.250	–29.500		–0.068	–0.087	–0.218
	308		–9.500	–13.250	–29.500		–0.073	–0.920	–0.238
	313		–12.90	–16.500	–41.500		–0.078	–0.096	–0.254
Na^+	298	+20	–2.600	–4.802	–13.500	+0.05	+0.0140	–0.002	–0.130
	303		–3.122	–6.802	–18.750		+0.0130	–0.007	–0.139
	308		–3.629	–8.755	–24.167		+0.0120	–0.014	–0.147
	313		–4.201	–10.795	–29.500		+0.0110	–0.020	–0.154
Ca^{2+}	298		–605	–847	–975	–1.35	–2.639	–3.422	–3.883
	303		–559	–827	–919		–2.519	–3.385	–3.698
	308		–513	–808	–855		–2.378	–3.370	–3.507
	313		–474	–790	–805		–2.222	–3.305	–3.342
Sr^{2+}	298		–924	–1170	–1280		–3.752	–4.560	–4.997
	303		–885	–1151	–1252		–3.614	–4.510	–4.810
	308		–840	–1135	–1177		–3.469	–4.463	–4.627
	313		–788	–1118	–1132		–3.312	–4.400	–4.445
Ba^{2+}	298		–1255	–1500	–1618	–1.9	–4.682	–5.452	–5.856
	303		–1212	–1479	–1565		–4.518	–5.401	–5.688
	308		–1162	–1459	–1503		–4.350	–5.349	–5.508
	313		–1110	–1439	–1452		–4.204	–5.300	–5.399
Cl^-	298	–220	–7.750	–11.500	–23.500	–0.75	–0.062	–0.082	–0.201
	303		–9.500	–13.250	–29.500		–0.068	–0.087	–0.218
	308		–11.100	–14.900	–35.500		–0.073	–0.092	–0.238
	313		–12.900	–16.500	–41.500		–0.078	–0.096	–0.254
Br^-	298		–4.250	–5.200	–6.500		–0.049	–0.055	–0.107
	303		–6.250	–7.000	–15.700		–0.055	–0.060	–0.139
	308		–8.000	–9.000	–25.700		–0.062	–0.067	–0.171
	313		–10.000	–11.000	–35.500		–0.067	–0.073	–0.203
I^-	298	–370	–1.500	–3.250	–4.000	–1.25	–0.035	–0.042	–0.057
	303		–3.350	–5.000	–8.000		–0.041	–0.048	–0.083
	308		–5.100	–6.800	–11.500		–0.049	–0.054	–0.109
	313		–7.000	–8.500	–15.500		–0.056	–0.060	–0.134

The ionic energies and ionic entropies are all negative except in case of Na^+ in 10% DMF-H_2O system. The ionic energies and ionic entropies for anions decrease in the order of $I^- > Br^- > Cl^-$ at any particular temperature. In case of cation the variation is in the order of $Na^+ > K^+ > Ca^{2+} > Sr^{2+} > Ba^{2+}$. In all cases, ionic parameters of viscous flow decrease with the increase in mole fraction of DMF in solvent.

As there is a direct connection between the entropy of certain single ion and the degree of order or disorder produced in the system, the standard entropies of ion in the DMF-H_2O system have been utilised for assessing the effect of particular ions on the structure of solvents of varying composition between the temperature range 298 and 313 K. The negative values for entropies indicate that ions have a net ordering effect on the studied solvent system.

The effect of ions on the bulkier DMF-H_2O mixed solvent molecule[9] can be clearly explained after ascertaining size and charge of ions together with their behaviour in aqueous solution and mixed solvent. In aqueous solution, anions are thought to cause chiefly structure breaking of the solvent[17]. In aqueous solution Br^- ion having low charge density and negative B-Coefficient is considered as weak structure breaker[17] while in DMF, the ion is slightly solvated because of low positive charge on the nitrogen of the DMF molecule and steric hindrance due to the presence of methyl groups[26, 27]. In the mixed solvent system, ΔS^*_{ion} are also negative as that in aqueous system but having slightly higher value probably due to combined effect. In aqueous solution ΔS^*_{ion} decreases with increase in ionic size *i.e.*, $\Delta S^*_{I^-}$ and $\Delta S^*_{Cl^-}$ whereas in mixed solvent the order is just reverse *i.e.*, $\Delta S^*_{I^-} > \Delta S^*_{Cl^-}$ indicating reversal of the behaviour of ions. Mixed solvent system has most stable transition state around iodide ion, probably due to large ionic size and low charge density which is more suitable for accommodation of bulkier mixed solvent molecules in its vicinity. Due to smaller size, Cl^- ion produces more distortion in solvent structure[9]. Study of partial molar volume data for chloride and bromide of barium in DMF-H_2O mixed solvent at 298 and 303 K have also given similar information regarding chloride and bromide ions[10, 11]. In case of cations, the order of changes of ionic entropies is reverse, smaller Na^+ has higher value than that of K^+ ion indicating that Na^+ helps much in maintaining the order of bulkier solvent structures. This is due to smaller size of ion and the surface charge density is not sufficiently large to orientate the solvent molecules immediately adjacent to ion. The positive value for ΔS_{Na^+} has also been reported by Nightingale and Benck[2] in aqueous solution at 298 K but the value is found to be lower in mixed solvent indicating an increasing effect of ion. The increment is $\Delta S^*_{K^+}$ ion in mixed solvent over that of aqueous solution can similarly be attributed as in case of halide ions. In case of divalent ions, ionic entropies decrease with ionic size. Ba^{2+} ion has the lowest ΔS^*_{ion} indicating its large ability for ion-solvation in mixed solvent system. The order of ion-solvation is $Ba^{2+} > Sr^{2+} > Ca^{2+}$, probably due to variation in crystal radius, charge density and hydration ability[20]. The values for Ca^{2+} and Ba^{2+} are lesser than the corresponding value in aqueous solution[2] suggesting that bulkier mixed solvent has less ordered structure in the vicinity of these ions. The variation of ΔS_{ion} with mole fraction of DMF in the solvent is shown in Fig. 1. These ions are minimally solvated in 40% DMF-H_2O mixture.

The extrapolation of curves for zero mole-fraction of DMF give the result for ionic entropy in pure water. For cations the values obtained are very close to that reported by Nightingale and Benck[2] but the values for anions differ markedly indicating that the behaviours of cations in mixed solvent are similar to that in aqueous solution.

Variation of temperature has also a marked effect on the ion- solvation in mixed solvent system. The variations of ΔE^*_{ion} and ΔS^*_{ion} with temperature are shown in Fig. 2. The decrease in ionic entropies with increase in temperature between 298 and 313 K for anions and univalent ions indicates the decrease in the extent of ion-solvation due to thermal agitation. In case of divalent ions, there is an increase in both ΔE^*_{ion} and ΔS^*_{ion} with the rise of temperature. This is probably due to charge effect, suitable orientation of solvent structures around ions and predominancy of hydration ability over structure breaking tendency of ions.

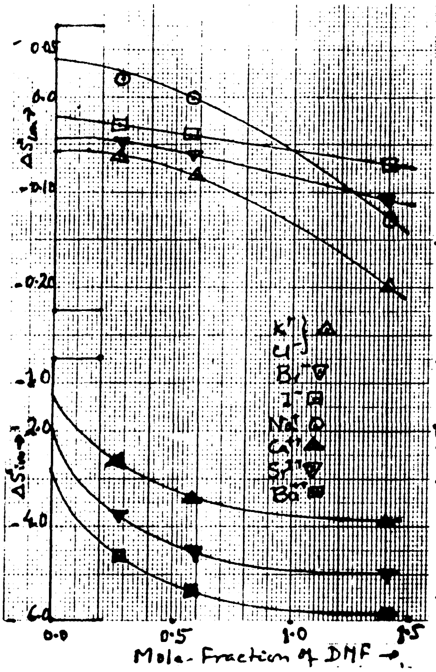

Fig. 1 Ionic activation entropy of viscous flow as a function of mole-fraction of DMF in solvent at 298 K

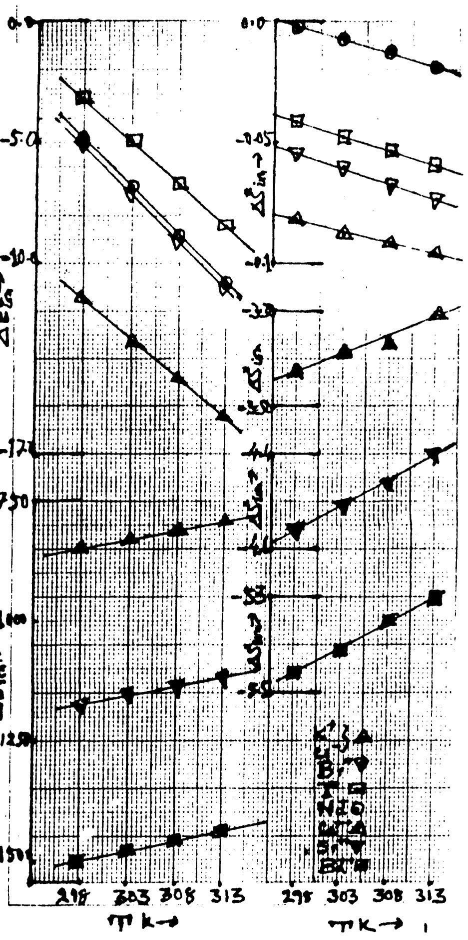

Fig. 2 Ionic activation energy and activation entropy of viscous flow in 20% DMF H_2O as a function of temperature

Similar interpretation regarding the order producing and order destroying ability of ions in mixed solvent system can be stated on the basis of B ion values and ionic activation energies of viscous flow but the explanations based on the concept of ionic activation entropies are more important and more informative and therefore this has mainly been considered in our discussion.

Ions	ΔS^{*}_{ion} (e.u.) (Nightingale and Benck, ref. 2)	ΔS^{*}_{ion} (e.u.) (Our value)
Na^+	+0.05	+0.04
Ca^{2+}	-1.35	-1.40
Sr^{2+}	—	-1.90
Ba^{2+}	-1.90	-2.40
K^+	-0.75	-0.060
Cl^-		
Br^-	—	-0.045
I^-	-1.25	-0.020

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