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Relative viscosities of metal formates in formic acid

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Abstract

The relative viscosities of formates of lithium, sodium, potassium, calcium and barium in formic acid have been determined at 30°C. The data has been analysed by Jones–Dole equation. The ionic B-coefficient values have been derived and quantitatively interpreted. Large and positive B-coefficient values and large values of solute-free energy of activation of flow parameter leads to the conclusion that the cations under study enhances the formic acid structure in the order: $Ba^{2+} > Ca^{2+} > K^+ > Na^+ > Li^+$. The solvation numbers of these ions in this solvent are also reported.

Key words: Relative viscosities, formic acid, metal formates.

1. Introduction

While ion-solvent interactions have been studied in detail in aqueous solutions, less consideration has been given to such effects in non-aqueous solvents. In a previous paper[1], we have reported the apparent molar volumes of some metal formates in formic acid of medium dielectric constant and concluded that the metal ions are solvated in this medium. In continuation of these studies B-coefficients have been measured for the formates of lithium, sodium, potassium, calcium and barium in formic acid and ionic B-coefficients have been determined and quantitatively interpreted. Further the solvation numbers of these ions in formic acid are calculated and their significance discussed in the present communication.

2. Experimental

Formic acid (Riedel, 98–100%) purified by the standard procedure[2] (density 1.2058 g/ml lit.[3] 1.2073 g/ml; viscosity 1.459 cp lit.[4] 1.465 cp) was used in these studies. Formates of lithium, sodium, potassium, calcium and barium were prepared by dissolving the metal carbonates (BDH, AnalaR) in AnalaR grade formic acid. The methods and apparatus used in the studies are the same as those already described in our earlier publication[5]. The reported viscosity data are reproducible within ±3% and the densities obtained are accurate to ±0.0002 g/ml. All the measurements were carried out at 30±0.01°C.

3. Results and discussion

The relative viscosities (η/η_0) of formates of lithium, sodium, potassium, calcium and barium in formic acid are determined at 30°C and are presented in Table I. The viscosity

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data has been analysed by means of Jones–Dole equation

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC. \tag{1}$$

'A' relates to the interionic interaction of the Debye–Huckel type and is calculated by using molar conductivities of ions and 'B' is closely related to ion-solvent interaction. The values of A and B-coefficients are obtained by fitting the experimental data by the method of least squares into the Jone–Dole equation. No change of slope with concentration was noticed in the concentration range above 0.1 g mole/litre.

Table I
Molar concentration (C) and relative viscosity (η/η_0) of salts in formic acid at 30°C

$C \times 10^3$ (g mole litre^{-1})	η/η_0	$C \times 10^3$ (g mole litre^{-1})	η/η_0
Lithium formate			
20.00	1.0141	165.10	1.0973
41.30	1.0213	206.30	1.1199
61.90	1.0384	247.70	1.1385
82.50	1.0565	288.80	1.1660
123.80	1.0957	330.10	1.1875
Sodium formate			
20.60	1.0112	206.30	1.1270
41.30	1.0172	247.60	1.1428
61.90	1.0406	288.80	1.1743
123.80	1.0745	330.10	1.1792
165.10	1.1016		
Potassium formate			
20.60	1.0155	165.10	1.1278
41.30	1.0314	206.30	1.1613
61.90	1.0480	247.60	1.1927
82.50	1.0639	288.80	1.2277
123.80	1.0945	330.10	1.2639
Calcium formate			
10.20	1.0108	40.80	1.0614
15.00	1.0220	51.00	1.0742
20.40	1.0400	61.20	1.0909
30.60	1.0490	71.40	1.0991
35.40	1.0509	81.60	1.1147
Barium formate			
11.20	1.0225	80.00	1.1207
28.80	1.0443	89.60	1.1325
40.00	1.0627	108.80	1.1633
48.00	1.0733	128.00	1.1935
70.40	1.1150	136.00	1.2129

Table II
Experimental (A) and theoretical (A_n) coefficients of salts in formic acid at 30°C

Salt	A $(\text{cm}^3\ \text{mole}^{-1})^{1/2}$	A_n $(\text{cm}^3\ \text{mole}^{-1})^{-1/2}$
HCOOLi	0.0263	0.0099
HCOONa	0.0240	0.0189
HCOOK	−0.0020	0.0004
$(\text{HCOO})_2\text{Ca}$	−0.0050	0.0001
$(\text{HCOO})_2\text{Ba}$	0.0415	0.0289

3.1 A-coefficients in formic acid

The A-coefficients of the salts in formic acid are calculated theoretically[6] from limiting equivalent conductance and physical properties of the solvent. The values are presented in Table II, along with the experimental values. On the basis of the values reported in literature[7] and on the basis of the assumption made in the theoretical calculations and the limitations of experimental techniques the difference between the A_{theo} and A_{expt} values is tolerable. From the results in Table II, it is observed that the 'A' values are positive for the formates of lithium, sodium and barium but negative for the formates of potassium and calcium. Although the negative values of K^+ and Ca^{2+} have no physical meaning, similar observations have been reported for some electrolytes in other non-aqueous solvents[8,9].

3.2 B-coefficients of the salts in formic acid

The B-coefficients are positive and high. The positive B-values suggest that these salts are structure makers in this solvent. The large value of B-coefficient in non-aqueous solvents is generally associated with the large molar volume of the latter with consequent increase in the solvated ionic radii[10].

It was mentioned by Feakins and Lawrence[11] that the positive B-coefficient results in the case of associated solvents due to both positive and negative contributions. The same arguments may hold good for present study in view of the fact that formic acid is an associated solvent.

Any variation in B-coefficient can be attributed to the cation since the anion is common for all the electrolytes. It may be observed from the values that for the salts under investigation, the B-coefficient

Salt:	HCOOLi	HCOONa	HCOOK	$(\text{HCOO})_2\text{Ca}$	$(\text{HCOO})_2\text{Ba}$
B value:	0.52	0.63	0.80	1.37	1.50

increases with the increase in the size of the cation. The size of the solvated metal ion varies as $Ba^{2+} > Ca^{2+} > K^+ > Na^+ > Li^+$. This shows that greater the size of the solvated ion, greater is the B-coefficient which provides further evidence for their

Table III
Values of $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ for salts in formic acid at 30°C

Salt	$\Delta\mu_1^{0\neq}$ (K cal mole^{-1})	$\Delta\mu_2^{0\neq}$ (K cal mole^{-1})
HCOOLi	11.52	19.67
HCOONa	11.52	21.06
HCOOK	11.52	23.95
$(HCOO)_2Ca$	11.52	34.60
$(HCOO)_2Ba$	11.52	35.02

structure-enhancing role in this medium. Such behaviour which is common in non-aqueous solvents, may be contrasted with the situation occuring with the large alkali metal cations in water, where low or negative values of B and positive dB/dt coefficients are found[12]. Thus for water, viscosity decrease due to disruption of solvent structure is evidently of much greater importance than for other solvents.

On applying the transition state theory and equating BC (Jones–Dole equation) with terms corresponding only to ion-solvent interactions, the expression for B has been found[13] to have the form:

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\left(\frac{\Delta\mu_2^{0\neq} - \Delta\mu_1^{0\neq}}{RT}\right) \tag{2}$$

where $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molar volumes of solvent and solute respectively at infinite dilution. $\Delta\mu_2^{0\neq}$ is the contribution per mole of solute to the free energy of activation for the viscous flow of the solution, and $\Delta\mu_1^{0\neq}$ is the free energy of activation per mole of the pure solvent given by the equation

$$\Delta\mu_1^{0\neq} = RT \ln\left(\frac{\eta_0 \bar{V}_1^0}{hN}\right). \tag{3}$$

The present viscometric data is analysed in terms of the above theory and the values of $\Delta\mu_1^{0\neq}$ and $\Delta\mu_2^{0\neq}$ are calculated and presented in Table III.

From the results in Table III, it is clear that $\Delta\mu_2^{0\neq}$ values are positive and much greater than $\Delta\mu_1^{0\neq}$ values. This shows that the formation of the transition state is less favoured in the presence of these salts. The variation of $\Delta\mu_2^{0\neq}$ is similar to the variation of B-value.

3.3 Ionic B-coefficients in pure formic acid

The anions of the type $HCOO^-$, being of the same size and character as the solvent molecules HCOOH, will have very little disturbing effect on the solution structure. Under these conditions the entire B-coefficient can be assigned to the cation cinvolved. Miyajima *et al*[14] in their study on the viscosity of aqueous solutions of sodium alkanoetes reported that for formate ion the value of B-coefficient and the temperature dependence

Table IV
Values of R_+ along with R_C (crystallographic radii) from B_+ values from Einstein equation

Ion	B_+	R_+ (A°)	R_C (A°)
Li^+	0.52	23.03	0.60
Na^+	0.63	21.83	0.95
K^+	0.80	20.10	1.33
Ca^{2+}	1.37	17.02	0.99
Ba^{2+}	1.50	16.30	1.35

of ionic B-coefficient (dB_{HCOO^-}/dt) are both zero. Similar thing is assumed in the present studies, the ionic B-coefficients will be 0.52, 0.64, 0.80, 1.37 and 1.50 for Li^+, Na^+, K^+, Ca^{2+} and Ba^+ ions respectively.

An analysis of B-coefficient is made using equation (4) which is proposed[15] on the basis of the hypothesis that the ion behaves like a rigid sphere (with $R\pm$ radius) moving in a continuum.

$$B_\pm = 2.5\left(\frac{4\pi}{3}\right)\frac{R_\pm^3\,N}{1000} \tag{4}$$

N is avogadro's number. 2.5 is the shape factor for a sphere. From $R_\pm$ values it is possible to say whether the ions are solvated or not, depending on whether or not the $R_\pm$ values are higher than the crystallographic radii for the ions concerned. The $R_\pm$ values obtained are given in Table IV together with the crystallographic radii. R_+ values are higher than the crystallographic radii. This leads to suppose that these ions in formic acid are solvated. It is observed that the R_+ values decrease from Li^+ to Ba^{2+} ion. This indicates that the obstruction to the solvent viscous flow increases with the increase of the ion charge density and hence with the increase of the size of the hydrodynamic entity by solvation.

The degree of solvation is calculated from B-coefficient values from equation (5)[11]

$$B_\pm = \frac{2.5}{1000}\,[V_i - nV_s] \tag{5}$$

V_i is the bare ion molar volume, V_s is the solvent molar volume and n, the number of the solvent molecules bound to the ion in the primary shell of solvation. The values obtained are 5.99, 7.08, 8.83, 14.10 and 16.01 for Li^+, Na^+, K^+, Ca^{2+} and Ba^{2+} ions respectively. Almost different values for the solvation of metal halides were reported in formic acid solutions using the conductivity method by Paul *et al*[16]. Their values for the three alkali metal ions are 6.6(Li^+), 4.0(Na^+) and 2.9(K^+). The difference between two sets may be due to the different experimental techniques as well as different experimental conditions.

Ionic B-coefficients in formic acid are also interpreted in terms of the local viscosities proposed by Stokes and Mills[17]. The coefficients obtained in this solvent are very much larger than those in water[12] and this may be attributed in part to the larger size of the solvent molecules. In accordance with this interpretation, this would lead to large η^E values for the solvated ions and η^A effect would also be greater resulting in fairly large positive value of B in formic acid which is actually observed.

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References

1. Subha, M. C. S., Chowdoji Rao, K. and Brahmaji Rao, S. — *Indian J. Chem.* 1986, **25A**, 424–426.
2. Weissberger, A. — *Technique of organic chemistry* (Vol. III), 2nd Edn., Interscience, New York, 1967, p. 389.
3. Washburn, E. W. — *International critical tables*, McGraw-Hill, New York, 128, **3**, 122.
4. Weast, R. C. — *Handbook of chemistry and physics*, 55th edn., The Chemical Rubber Co., Cleveland, Ohio, 1974.
5. Chowdoji Rao, K. and Brahmaji Rao, S. — *Indian J. Chem.*, 1980, **19A**, 467; 1982, **21A**, 71.
6. Falkenhagen, H. and Vernon, E. L. — *Phys. Z.*, 1932, **33**, 140; *Philos, Mg.*, 1932, **14**, 537.
7. Gill, D. S. and Sharma, A. N. — *J. Chem. Soc. Faraday Trans. I*, 1982, **78**, 475.
8. Blokhra, R. L. and Parmar, M. L. — *Z. Phys. Chem. N.F.*, 1975, **95**, 310.
9. Blokhra, R. L. and Verma, P. C. — *Electrochim. Acta.*, 1977, **22**, 1101.
10. Nightingale, E. R. and Benck, R. F. — *J. Phys. Chem.*, 1959, **63**, 1777.
11. Feakins, D. and Lawrence, K. G. — *J. Chem. Soc. A*, 1966, 212.
12. Chowdoji Rao, K. — *Thermodynamic study in liquid mixtures* (A study of physico-chemical properties of metal formates in binary liquid mixtures of formic acid), Ph.D. Thesis, Sri Krishnadevaraya University, Anantapur, 1984.
13. Feakins, D., Freemantle, D. J. and Lawrence, K. G. — *J. Chem. Soc. Faraday Trans. I*, 1974, **70**, 795.
14. Miyajima, K., Sawada, M. and Nakagaki, M. — *Bull. Chem. Soc. Jap.*, 1982, **55**, 3101.

15. Einstein, A. *Ann. Phys.*, 1906, **19**, 289; 1911, **34**, 591.

16. Paul, R. C., Sharma, R., Puri, T. and Kapoor, R. *Aust. J. Chem.*, 1977, **30**, 535.

17. Mills, R. and Stokes, R. H. *Viscosities of electrolytes and related properties*, Pergamon, New York, 1965.