TABLE 4 — INTERACTION ENERGY PARAMETER (X_{12}) AT EQUIMOLAR CONCENTRATION FOR VARIOUS BINARY MIXTURES

Binary mixture of 1,4-dioxane with	ΔH(J/mol)	X_{12}(J/mol)
Toluene	123.2	6.69
Ethylbenzene	277.5	14.23
Cyclohexane	1625.3	85.44
Methylcyclohexane	1638.7	81.59
n-Heptane	1801.3	80.33

from the densities of pure components between 293.15 K and 303.15 K, γ is given by the simple relation[7]

$$\gamma = 1/T \left(\frac{\Sigma n_i a_i}{V_m} \right)^2 \qquad ...(3)$$

where V_m is the molar volume of the liquid at temperature T, a_i is a value characteristic of a given atom or atomic grouping and n_i represents the number of a_i per mole of the liquid. The values of a_i for various atomic groupings have been tabulated by Manzini et al.[7] and the same have been used to determine values at 300.05K. The values of α, γ and V_m for the pure components are given in Table 3.

The values of X_{12} (given in Table 4) were determined for each mixture by fitting Eq. (4)

$$\Delta H = \left[\frac{x_1 p_1^* V_1^*}{V_1} + \frac{x_2 p_2^* V_2^*}{\tilde{V}_2} \right] -$$
$$\left[\frac{x_1 p_1^* V_1^* + x_2 p_2^* V_2^*}{\tilde{V}} \right] +$$
$$\left[\frac{x_1 \theta_2 V_1^*}{\tilde{V}} \right] X_{12} \quad ... (4)$$

to the smoothened experimental ΔH at 0.5 mol fraction. Using the values of X_{12} and Eq. (4), enthalpy changes for the various binary systems studied in this work have been calculated at intervals of 0.05 mol fraction. These ΔH values have been compared with experimental values of ΔH. It is observed that except for 1,4-dioxane + cyclohexane and + n-heptane systems the agreement between the experimental and theoretical values of ΔH is fairly good (Fig. 1). Even when there is disagreement between the theory and experiment, the order of magnitude of the two sets of values is not very much different.

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Conductance Behaviour of Sodium, Potassium & Calcium Formates in Aqueous Organic Solvents[†]

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Conductances of sodium, potassium and calcium formates in formic acid-water mixtures differ from those in methanol-water mixtures. The conductance behaviour has been explained in terms of the associated nature of the solvent and the effective concentration of the ions. The factor, N^2 (N = total number of molecules of solvent mixture) represents the combined effects due to viscosity and effective concentration of ions. The deviations observed in aqueous formic acid beyond 30% formic acid are attributed to the complex formation between the organic co-solvent and H_2O.

STUDIES[1,2] on ion-solvent interactions in aqueous-organic solvent binary mixtures have shown that in the water-rich region, an enhanced structure due to hydrophobic hydration[3] or a continuous disruption of the water lattice[4] occurs. It is known that the viscosity of mixed solvents increases due to the formation of polymeric species. The ionic conductance of highly solvated ions in these solvent mixtures is not expected to be influenced[5,6] by this enhanced viscosity. But the conductance may diminish linearly with N^2 (N = total number of moles of mixed solvent) due to combined effect of the increase in the viscosity of hypothetical monomers present in the liquid mixture and the increase in the effective concentration of the ions. To study the effect of formic acid and methyl alcohol on the conductance of sodium, potassium and calcium formates in water, we have determined equivalent conductances of these salts at different compositions of aqueous organic solvents and the results are presented in this note.

All the chemicals employed were of AR grade. The solvents were purified by the standard methods[7]. The specific conductances of formic acid, methanol and water were less than 6.1×10^{-5}, 0.73×10^{-5} and 1.0×10^{-6} Ω cm^{-1} respectively. The conductance measurements were made with a Philips (India) conductivity bridge type PR 9500 using a cell of constant 0.9546. The procedures employed for the measurement of the density and viscosity were the same as reported earlier[8]. The densities and viscosities of water-methanol mixtures were taken from the literature[9].

The ionic conductances for the metal ions and chloride ion in the organic solvent mixtures used were calculated by dividing the equivalent conductances of their salts by the ratio of the ionic conductances of the constituent ions in aqueous medium. The ionic conductances in water were evaluated from the equivalent conductances of chlorides and the metal ions and the transport numbers reported in literature[10].

The experimental data obtained are presented in Tables 1-3. It is seen from these results that the conductances of the formates in formic acid-water mixtures are greater than those in methanol-water mixtures. However, the same trend, namely $Ca^{2+} >$ $K^+ > Na^+$ is observed in either mixture.

It is known that liquid water, composed of octomers and dimers, gets modified in presence of organic liquids. However, cations capable of undergoing heavy hydration displace the organic solvent molecules. Hence the alkali metal ions Na^+, K^+ and Ca^{2+} in aqueous organic solvents are expected to have the nearest solvent sheath containing water molecules. The conductance is therefore expected to diminish with the decrease in the water content of the solvent medium. It is seen from the typical plots between conductance and N^2 (Fig. 1a & b) that a linear decrease is obtained up to 50% (v/v) methanol in the case of aqueous methanol while a linear increase up to 30% (v/v) formic acid and a linear decrease beyond 30% formic acid is noticed in the case of aqueous formic acid mixtures. Similar plots were found in other cases. These facts suggest that methyl alcohol functions as a structure breaker while formic acid behaves as a structure maker since alkali metal ions are known as structure breakers. However, the trend beyond 30% formic acid is opposite to that observed up to 30% formic acid. This may be attributed to complex formation between formic acid and water beyond 30% (v/v) formic acid.
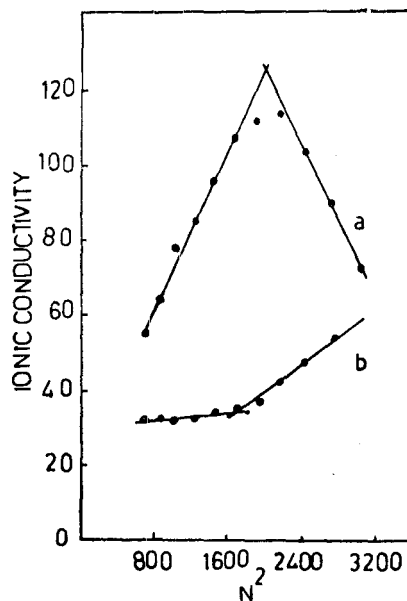

Fig. 1 — Plot of ionic conductivity vs N^2 for (a) potassium ion in H_2O-HCOOH and (b) potassium ion in H_2O—CH_3OH

TABLE 1 — DENSITY (d), VISCOSITY (η) AND SPECIFIC CONDUCTANCE (κ) OF HCOOH-H_2O & MeOH—H_2O MIXTURES AT 35°C

Organic solvent (%, v/v)	d (g. ml⁻¹)	η (Cp)	κ (Ωcm^{-1})
		FORMIC ACID-H_2O MIXTURE	
0	0.9941	0.718	1.12
10	1.0155	0.768	6.41
20	1.0385	0.807	11.73
30	1.0585	0.850	12.33
40	1.0776	0.896	12.10
50	1.1001	0.955	10.06
60	1.1680	0.994	8.68
70	1.1304	1.050	7.34
80	1.1506	1.116	5.46
90	1.1620	1.174	3.90
100	1.1780	1.234	2.34
		METHANOL*-H_2O MIXTURE	
0	0.9941	0.980	1.12
10	0.9763	1.158	1.65
20	0.9598	1.400	1.24
30	—	—	1.14
40	0.9249	1.593	0.80
50	0.9049	—	0.73
60	0.8828	1.403	0.73
70	—	—	0.73
80	0.8336	1.006	0.73
90	0.8057	0.767	0.73
100	0.7771	0.545	0.73

*d Values are at 25°C

TABLE 2 — EQUIVALENT CONDUCTANCE OF SALT SOLUTION (0.05M) IN HCOOH-H_2O & MeOH-H_2O MIXTURES AT 35°C

Organic solvent (%, v/v)	HCOONa	HCOOK	$(HCOO)_2Ca$	NaCl
		FORMIC ACID-H_2O MIXTURE		
0	109.1	119.4	190.9	131.7
10	112.3	181.8	200.9	293.7
20	127.3	212.1	238.6	334.9
30	136.4	231.5	254.5	337.9
40	134.4	230.0	254.5	320.9
50	130.8	222.0	246.3	299.0
60	120.8	200.9	231.5	254.6
70	112.3	173.4	205.6	218.2
80	100.5	159.1	190.9	181.8
90	90.9	131.6	166.0	146.9
100	83.9	112.3	141.5	95.5
		METHANOL-H_2O MIXTURE		
0	109.1	119.4	190.9	131.7
10	95.5	109.2	146.9	112.3
20	83.0	95.6	123.2	97.9
30	74.9	86.8	103.2	86.8
40	68.2	76.4	90.9	79.6
50	62.6	73.4	79.6	70.7
60	59.7	70.8	70.7	70.7
70	58.7	66.0	61.6	70.7
80	58.7	66.0	—	68.2
90	58.8	66.0	—	67.0
100	56.2	66.0	—	68.6

TABLE 3 — THE IONIC CONDUCTANCE OF Na^+, K^+, Ca^{2+} AND Cl^- IN FORMIC ACID-WATER AND METHANOL-WATER MIXTURES

Ion	Formic acid (%, v/v)		Methanol (%, v/v)	
	30%	90%	50%	70%
Na^+	133.8	58.2	28.0	28.0
K^+	113.5	64.5	30.6	32.4
Ca^{2+}	45.2	72.7	34.9	27.0
Cl^-	172.2	74.9	36.0	36.0

An attempt has been made to substantiate this with the help of Grunberg's d' parameter[11] and the excess viscosity η^E. The values of these parameters are positive and change in magnitude up to 40% (v/v) of formic acid as expected for complex formation [η^E = 0.033, 0.053, 0.060, and 0.060; d' = 0.611, 0.494, 0.391 and 0.382 in 20, 40, 60 and 80% HCOOH respectively].

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Viscosities of Binary Liquid Mixtures of Formic Acid with Water, Methanol, Acetonitrile & Dimethylformamide

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The excess viscosity (ηE), molar free energy of activation of flow ($g*E$), the interaction strength term (d') of Grunberg and Nissan equation and the interaction energy term (W_{visc}) of Katti and Chaudhri have been calculated from the densities and viscosities of the binary liquid mixtures of formic acid with water, methanol, acetonitrile and dimethylformamide at 30°C. It is observed that non-specific dipolar interactions are only present in formic acid + methanol and formic acid + acetonitrile mixtures while strong specific interactions are present in formic acid + dimethylformamide and formic acid + water mixtures. These specific interactions are attributed to the formation of molecular complexes (3:1 and 1:1 respectively) between the components.

EVENTHOUGH attempts have been made to study the molecular interactions in binary liquid mixtures containing formic acid, through the measurement of exess thermodynamic functions, not many reports[1] are there using the viscosity data. The present note deals with the study of these interactions at 30°C in the title binary liquid mixtures in terms of excess viscosity (η^E), excess molar free energy of activation of flow ($g*^E$), the interaction strength factor of Grunberg and Nissan[2] (d') and interaction energy term (W_{visc}) of Katti and Chaudhri[3].

The liquids were purified by the standard procedures[4] and the measured densities and viscosities are in good agreement with the literature values[5,6]. The literature values[7] of density (0.9957 g/ml) and viscosity (0.8007 cp) at 30°C of water were used in the calculations.

Mixtures of known compositions were prepared by weight and the viscosities determined by the relative method of Ostwald. Densities were measured with a pyknometer of 25 ml capacity.

The values of η, η^E, $g*^E$, d^1 and W_{visc} calculated from the viscosity data are presented in Table 1.

The viscosities of the mixtures varied non-linearly with composition indicating a non-ideal behaviour. The variations of η^E and $g*^E$ with mol fraction of formic acid indicates a maximum in both the parameters in the case of formic acid + water (FA+W) and formic acid + dimethylformamide (FA+DMF) systems. The positive values of η^E with a marked maximum indicates strong unlike interactions resulting in the formation of a complex[8]. The composition of the complexes is 3:1 (FA:DMF) and 1:1 (FA:W) respectively. The higher positive η^E values for FA + DMF mixture suggests that the complex formed in this system is more stable than that between FA and W. Similar behaviour was reported by Solimo and coworkers in the case of binary liquid mixtures of propionic acid[9] with aniline, pyridine and dimethylaniline.

The negative values of η^E in the case of formic acid + methanol (FA + M) and formic acid + acetonitrile (FA + AN) suggest that dispersion forces are dominant in these systems. Similar trend was reported by Katz et al.[10] in the case of binary liquid mixtures of aniline with toluene and butanol.

The FA + M system is having greater $g*^E$ values than the FA + AN system (Table 1). This situation is reverse of that observed in the case of η^E values. This could be attributed to the influence of viscosity (η) and molar volume (V) simultaneously[11]. The non-zero value of d' indicates the non-ideal behaviour of the mixtures. The trend in d' values is almost the same as that in η^E values.

The large negative values of W_{visc} in the case of FA + M and FA + AN systems show an appreciable dipole-dipole interaction between the components, while the positive values in FA + W and FA + DMF systems show weak interactions. Dimethylformamide, methanol and water are associated in the pure state while acetonitrile is not. Addition of formic acid to these liquids is expected to cause similar changes. However methanol-formic acid mixture exhibits different behaviour.