TABLE 2 — EMF DATA AND SOLVENT TRANSPORT NUMBER, $\triangle$, FOR SILVER BROMATE AND SILVER IODATE IN WATER-ACETONITRILE MIXTURES AT 30°C

Mole fr. of acetonitrile X_{AN}	$\dfrac{\partial \ln f_{AN}}{\partial \ln X_{AN}}$	AgBrO$_3$		AgIO$_3$	
		$-E$(mV)	$\triangle$	$-E$(mV)	$\triangle$
0.05	0.52	26.0	0.99	38.0	1 44
0.15	0.75	11 0	2.10	12 5	2.44
0.25	0.87	5.3	2.93	8.1	4.47
0 35	0.89	3.1	2.46	7.8	6.18
0.45	0.87	5.3	3.87	11.5	8.39
0.55	0.82	8.2	4.32	14.2	7.48
0.65	0.75	13.3	4.64	16.6	5.79
0.75	0.67	16.3	3.55	12.0	2.61
0.85	0.41	21.0	1.74	16.0	1.32
0.95	0.21	23.5	0.54	10.0	0.23

ted it to the pyramidal structure of these ions with the halogen at the apex.

The solvent transport number, $\triangle$, of acetonitrile in these mixtures was calculated from the e.m.f. data on the cell described earlier[8] using the expression (3)

$$E = -\frac{RT}{F} \cdot \frac{(X''_{AN} - X'_{AN})}{X_{AN}(1 - X_{AN})} \cdot \triangle \cdot \left(1 + \frac{\partial \ln f_{AN}}{\partial \ln X_{AN}} \right) \quad ..(3)$$

where the various terms have their usual significance[7]. The last term in Eq. (3) was calculated from the vapour pressure data of water-acetonitrile mixtures taken from literature[13]. These data together with the e.m.f. of the cell used and the $\triangle$ values of acetonitrile for the two salts are given in Table 2.

It is seen that the $\triangle$ values are positive throughout and pass through a maximum at $X_{AN} = 0.65$ ($\triangle = 4.6$) for silver bromate and $X_{AN} = 0.45$ ($\triangle = 8.4$) for silver iodate. Thus there is an increase of 4. 6 mol and 8.4 mol of acetonitrile for silver bromate and silver iodate resectively per Faraday relative to the mean molar velocity of the solvent mixture as reference[14] in the cathode compartment when solutions of these salts are electrolysed in acetonitrile-water mixtures at the given compositions. The large positive $\triangle$ values in these mixtures for both salts are in agreement with the conclusions arrived from the transfer energy data of the salts earlier. The transport of acetonitrile into the cathode compartment occurs largely through silver ion while the anion transports water in the opposite direction. These two effects add together and thus a heteroselective solvation is characterised by large values of $\triangle$ as observed in the present case.

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Viscosities of Sodium Formate in Water & In Aqueous Formic Acid at Different Temperatures

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The viscosities of solutions of sodium formate (4×10^{-3}—$4 \times 10^{-1}M$) in water and in water-formic acid mixtures are measured at 30°, 35°, and 40°C and the data analysed by Jones-Dole equation. In the case of purely aqueous solutions, B-coefficient is positive and increases with increasing temperature indicating that sodium formate behaves as a structure breaker in pure water. But in the case of water-formic acid mixtures sodium formate behaves as a structure maker in mixtures containing formic acid greater than 40% (v/v).

IN the present note, viscosities of solutions of sodium formate in water and in aqueous formic acid (20, 40, 60, and 80% v/v) have been measured at 30°, 35°, and 40°C and B-coefficient values of Jones-Dole equation have been evaluated to obtain information about the nature of solute-solvent interaction.

Formic acid (Riedel, 98–100%) was purified by the standard procedure[1]; density 1.2058 g/ml (lit.[2] 1.2073 g/ml); η, 1.459 cP (lit.[3] 1.465 cP). Sodium formate used was of AR grade. Triply distilled water (Sp. cond. 2.8×10^{-6} ohm^{-1} cm^{-1}) was used as a standard liquid and for preparing the solutions.

The aqueous mixtures of formic acid were made using volume percentages. Densities of solutions were measured with a calibrated pycnometer with an accuracy of $\pm$ 0.0002 g/ml. Viscosities having accuracy of $\pm$ 0.3% were measured with a Ostwald type viscometer having a flow time of 265 $\pm$ 0.2 sec for water at 30°C. The temperature was controlled with an accuracy of $\pm$ 0.05°C.

The data relating to experimental density ρ, viscosity η, and relative viscosity (η_s/η_0) of solutions of sodium formate of different concentrations in water and in aqueous formic acid mixtures were obtained at 30°, 35° and 40°C. The viscosity data have been analysed by means of Jones-Dole equation $\eta_s/\eta_0 = 1 + A \sqrt{C} + BC$, values of the constants A and B have been graphically estimated from the intercept and slope respectively of the linear plots of $(\eta_s/\eta_0 - 1)/C^{1/2}$ versus $\sqrt{C}$. The plots of sodium formate in various percentages of formic acid at 30°, 35°, and 40°C are shown in Figs. 1, 2 and 3 respectively. The values of A and B are presented in Table 1.

The relative viscosity increases with increasing concentration. 'A' parameter for aqueous solutions is found to be (0.009 ± 0.0009) and agrees reasonably well with the values reported by Blokhra and Verma[4]. The positive temperature coefficient of B-parameter suggests that the sodium formate behaves as a structure breaker in pure water.

In the case of solutions containing 20-60% formic acid, the values of A are negative and such negative A values where reported in most of the cases involving mixed solvents[5,6]. However, the negative magnitude of A cannot be interpreted on the basis of Falkenhagen theory[7].

The dB/dT values are positive upto 40% formic acid and are negative at higher percentages ($> 40\%$) of formic acid. This indicates that the sodium formate behaves as a structure breaker in aqueous

Fig. 1 — Plot of $(\eta/\eta_0 - 1)/C^{1/2}$ versus $C^{1/2}$ of sodium formate in various percentages of formic acid at 30°C.

TABLE 1 — VALUES OF PARAMETERS A AND B FOR SODIUM FORMATE IN WATER AND IN AQUEOUS FORMIC ACID MIXTURES AT DIFFERENT TEMPERATURES

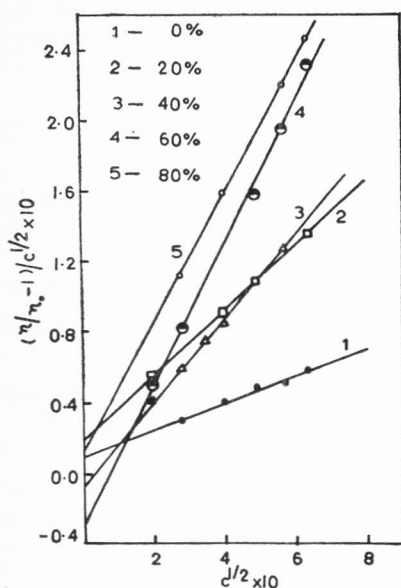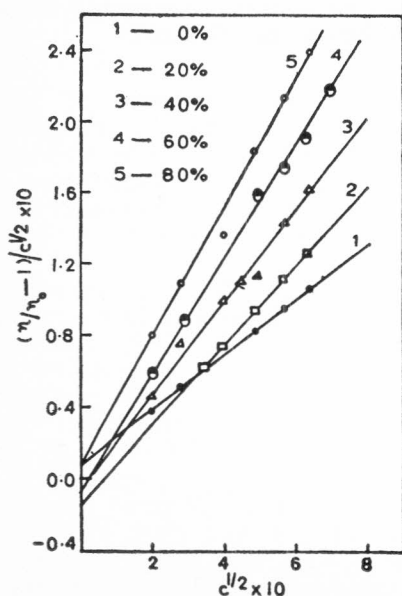| Water containing HCOOH (%, v/v)	Temp. (°C)	A	B
Nil	30	0.01	0.08
	35	0.01	0.15
	40	0.01	0.16
20	30	+0.02	0.16
	35	—0.02	0.21
	40	—0.03	0.24
40	30	—0.01	0.23
	35	—0.01	0.25
	40	—0.02	0.26
60	30	—0.03	0.39
	35	—0.01	0.34
	40	—0.03	0.32
80	30	+0.01	0.38
	35	0.01	0.35
	40	0.02	0.33

Fig. 2 — Plot of $(\tau/\eta_0 - 1)/C^{1/2}$ versus $C^{1/2}$ of sodium formate in various percentages of formic acid at 35°C.

Fig. 3 — Plot of $(\eta/\eta_0 - 1)/C^{1/2}$ versus $C^{1/2}$ of sodium formate in various percentages of formic acid at 40°C
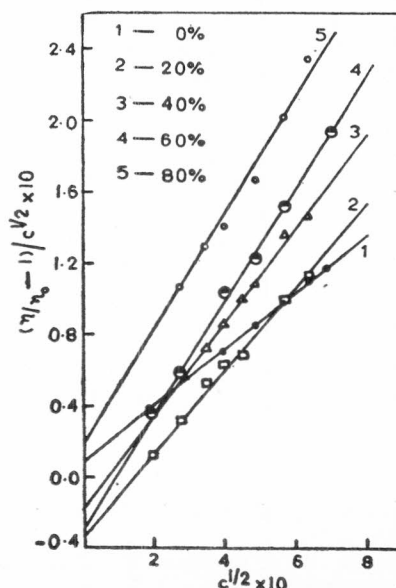
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TABLE 2 — VALUES OF EXCESS VISCOSITY (η^E), d^1 AND ACTIVATION ENERGY (E_η) FOR DIFFERENT AQUEOUS FORMIC ACID MIXTURES AT 35°C

Water containing HCOOH (%, v/v)	η^E	d^1	E_η (J. mol^{-1})
0	—	—	3.46
20	0.033	0.611	3.79
40	0.053	0.494	4.21
50	—	—	3.82
60	0.060	0.391	3.79
80	0.060	0.382	3.74

formic acid solutions containing less than 40% formic acid (v/v) and as a structure maker in solutions containing formic acid greater than 40%.

An attempt is made to explain the above results in terms of the parameter, d', suggested by Grunberg and Nissan[8]. The data relating to d^1 and excess viscosity

$$\eta^E = [\eta_{mix} — (x_1\eta_1 + x_2\eta_2)]$$ are given in Table 2.

The values of d^1 are positive and decrease with increase in formic acid content upto 40% and remain almost constant thereafter. It is also observed that the values of η^E are positive and increase with increase of formic acid upto 40% and thereafter remain almost constant. These trends indicate the existence of some type of complex formation between water and formic acid in water-formic acid mixtures containing formic acid upto 40%. The positive temperature coefficients in these solutions therefore, indicate the decrease of these specific interactions when sodium formate is added.

The constancy of B values in water-formic acid mixtures containing higher percentages ($> 40\%$) of formic acid suggests that the ordering effect in the solvation sphere has reached a stage such that the outer most layer has the same structure and composition as that of the solvent.

The values of activation energy, E_η, for the viscous flow are calculated from Eq. (1) and the values are recorded in Table 2.

$$\eta = A.e^{E\eta/RT} \qquad \dots (1)$$

E_η can be related to the work need to form vacant sites[9] in the solvent matrix, and may be regarded as a measure of the structure of the solvent. From the data in Table 2, it is observed that the E_η values remain almost constant for water-formic acid mixture containing more than 40% (v/v) formic acid. The values of B, d^1, η^E and E_η thus clearly suggest that sodium formate is not able to bring about any effective change in the solvent structure beyond 40% of formic acid.

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Reduction of Aquonickel(II) Complex in Presence of Alkaline Earth Metal Cations at the Dropping Mercury Electrode

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The polarographic behaviour of the aquonickel(II) complex has been investigated in the presence of $0.1M$ Mg(NO$_3$)$_2$, Ca(NO$_3$)$_2$, Sr(NO$_3$)$_2$ and Ba(NO$_3$)$_2$. Polarographic characteristics ($E_{1/2}$, i_d, D, α and slope) as well as double layer parameters (E_{max}, q_m, ψ'-potential, etc.) have been determined. Activation energy of rearrangement (Q_e) and activation energy of diffusion, Q_D, have been calculated by Vleek's method. The variation of polarographic characteristics has been explained on the basis of the change of double layer structure with the change of alkaline earth metal cation from Mg^{2+} to Ba^{2+}.

POLAROGRAPHIC reduction of the aquonickel(II) complex in aqueous non-complexing base electrolytes like chlorides of alkali metal cations was reported by us earlier[1]. As an extension, the results of title investigation are reported in this note.

All the reagents used were of AR grade. The concentration of nickel(II) nitrate was $2.5 \times 10^{-4}M$ in each case.

Polarograms were recorded at the desired temperature with a manual polarographic circuit. The cell resistance was measured with the usual type of a.c. Wheatstone bridge. The resistance varied within the range 1000 ± 100 ohms and therefore no iR correction was needed. Other experimental details were the same as described earlier[1,2]. Characteristics of d.m.e. were determined at three different heights of mercury column. One set of such data in $0.1M$ Mg(NO$_3$)$_2$ at open circuit are given below : $h = 40$ cm ; $t = 2.7$ sec ; $m = 3.19$ mg sec^{-1}.

The current-voltage (C-V) curves for the electro-reduction of the aquonickle(II) complex at all tempe-