The electronic spectra of thio compounds show three characteristic bands with the molar absorptivities of the order of 10^4 at 465, 317 and 214 nm in the case of tetrathiomolybdate and at 389, 274 and 214 nm in the case of tetrathiotungstate. These high-intensity bands are due to charge-transfer and are assigned to the transitions $t_1 \rightarrow 2e(\nu_1)$, $t_1 \rightarrow 4t_2(\nu_2)$ and $3t_2 \rightarrow 2e(\nu_3)$ respectively according to the Viste-Gray MO scheme[10]. The νM-S frequencies in the IR are reported to appear[11] in the range 450-500 and around 180 cm^{-1} for the thiomolybdates and thiotungstates. The strong intensity IR absorptions observed at 476, 462 and 195 cm^{-1} for thiomolybdate and 488, 466 and 187 cm^{-1} for thiotungstate salts are assigned to M-S stretching frequencies in the present compounds.

The thermal studies of the thiosalts were carried out, both, in air and nitrogen atmosphere. The two compounds exhibited similar decomposition behaviour for a particular atmosphere and the thermal behaviour was similar to that of ammonium[12] and morpholinium[4] tetrathiometallates. The salts decompose in two distinct steps, the first involving the formation of trisulphides and the second step involving its subsequent decomposition. Both in air and nitrogen, the salts start decomposing around 180° giving hydrogen sulphide as one of the gaseous products. The first stage of decomposition is complete by 350°. The weight losses noticed at this stage in both the atmospheres are 57 and 48% respectively for the thiomolybdate and thiotungstate. The expected weight losses for the formation of trisulphides are 57·9 and 48·5% respectively. On further increase in temperature, the trisulphides start decomposing in air to give the metal trioxides around 500°. The weight loss curves indicated 68 and 57% loss for the thiomolybdate and the thiotungstate and the expected weight losses for the formation of $M^{VI}O_3$ are 68·5 and 57·4% respectively. In nitrogen atmosphere, the weight loss recorded around 500° for N-ethylmorpholinium thiomolybdate was 65% and that for the corresponding thiotungstate was 54%. The calculated weight losses for the formation of corresponding metal disulphides are 64·9 and 54·6% respectively. The chemical and X-ray analyses confirmed the formation of $M^{VI}O_3$ in air and $M^{IV}S_2$ in nitrogen atmospheres.

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Physico-chemical Properties of Vegetable Proteins : Part IV— Flocculation of Protein Sols Stabilized at Different *p*H Values by Electrolytes

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Flocculation of a few vegetable protein sols stabilized at *p*H 11 and 7·5 by different electrolytes has been studied. The higher flocculation values are obtained for cations like Ca^{2+}, Sr^{2+} and Ba^{2+}, while lower values are obtained for cations like Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Ag^{+}. Protein fractions obtained with aq. NaCl yield more stable sols than the whole proteins etxracted from the same source with aq. NaOH. The flocculation values of various electrolytes for the sols stabilized at *p*H 2·5 show that amongst anions of a given valency, the one with a larger size is a more effective flocculent.

SEVERAL investigations relating to flocculation of sols of animal proteins such as haemoglobin[1], egg albumin[2], gelatin[2,3] and casein[4,5] by electrolytes have been reported in the literature. Similar work on vegetable proteins, however, has not received adequate attention. This prompted us to undertake the present work.

Two varieties of soybean proteins and their respective glycinin fractions; peanut protein and its major fractions (arachin and conarachin), and gliadin and glutenin fractions of wheat protein (gluten, BDH) were used. The methods employed for the isolation of these proteins were the same as described earlier[6].

Sols of 0·5% concentration at *p*H 11 and 7·5 were prepared by suspending the required amounts of proteins in 20 ml of CO_2-free dist. water, and adding enough of NaOH solution gradually with continuous stirring to dissolve the protein and raise the *p*H to about 11·5 in one set of experiments and to *p*H 8 in the second set. The excess of the alkali was removed by dialysis till the *p*H was brought down to 11·0 in the first case and 7·5 in the second case. Sols were also prepared at *p*H 2·5 following the same procedure except for using dil. HCl in place of NaOH.

Two ml aliquots of a given sol were added to several 3 ml portions of the solutions of increasing concentrations of a given electrolyte, and after shaking allowed to equilibrate at 30° ± 0·01° for 10 min. The minimum concentration of the electrolyte at which the turbidity appeared was noted. The process was repeated several times.

The flocculation values of different electrolytes, expressed as moles/10^5 g protein, for the sols of 0·5% concentration are presented in Table 1. The flocculation values for the sols at *p*H 7·5 are much lower as compared to the values at *p*H 11·0 because of a much smaller number of acid groups ionizing at this stage[7]. Since the protein sols carry negative charge

Table 1 — Flocculation Values of Different Electrolytes for Vegetable Protein Sols of 0·5 per cent Concentration at *p*H 11 and 7·5

Electrolyte	Flocculation values (moles/10^5 g protein)								
	Whole Punjab soybean No. 1 protein	Punjab soybean No. 1 glycinin fraction	Whole Bragg soybean protein	Bragg soybean glycinin fraction	Whole peanut protein	Peanut arachin fraction	Peanut conarachin fraction	Wheat gliadin fraction	Wheat glutenin fraction
$CaCl_2$	187 (97)	229 (119)	206 (116)	252 (128)	153 (116)	187 (117)	275 (125)	160	—
$SrCl_2$	150 (94)	220 (115)	160 (112)	247 (120)	148 (109)	175 (110)	250 (122)	120	—
$BaCl_2$	135 (91)	209 (110)	153 (110)	242 (116)	153 (106)	157 (107)	196 (117)	100	—
$ZnCl_2$	48 (17)	59 (22)	49 (22)	60 (28)	43 (16)	48 (17)	59 (24)	21	32
$CoCl_2$	47 (16)	58 (25)	50 (25)	60 (33)	43 (24)	48 (27)	63 (31)	20	29
$NiCl_2$	47 (18)	51 (27)	49 (23)	55 (32)	41 (18)	43 (19)	60 (20)	26	30
$CuCl_2$	46 (14)	56 (21)	46 (18)	59 (28)	46 (16)	47 (16)	65 (20)	20	35
$HgCl_2$	40 (16)	50 (24)	45 (19)	55 (27)	49 (19)	50 (20)	60 (25)	25	35
$AgNO_3$	130 (76)	142 (84)	142 (83)	153 (96)	168 (61)	175 (63)	192 (84)	37	50

Values in parentheses represent flocculation values of various protein sols stabilized at *p*H 7·5.

Table 2 — Flocculation Values of Different Electrolytes for Vegetable Protein Sols of 0·5 per cent Concentration at *p*H 2·5

Electrolyte	Flocculation values (moles/10^5 g protein)						
	Whole Punjab soybean No. 1 protein	Punjab soybean No. 1 glycinin fraction	Whole Bragg soybean protein	Bragg soybean glycinin fraction	Whole peanut protein	Peanut arachin fraction	Wheat gliadin fraction
Na_2HPO_4	125	156	150	168	150	160	90
$K_2Cr_2O_7$	130	150	140	156	100	110	60
Na_3AsO_3	210	256	250	287	255	260	150
Na_2SO_4	1106	1549	1382	1770	420	443	175
$K_3Fe(CN)_6$	25	25	30	31	20	25	15
$K_4Fe(CN)_6$	15	19	19	25	12	15	10

at these *p*H values, the cations of the electrolytes are more effective in causing the coagulation. However, the ordinary valency rule in determining the flocculating power of a cation does not appear to be valid. The electrolytes, in fact, may be divided broadly into two categories: the salts of alkaline earth metals (Ca, Sr and Ba), the flocculation values of which are fairly high, and the salts of transition metals, the flocculation values of which are relatively low. It appears that while the action of Ca^{2+}, Sr^{2+} and Ba^{2+} ions causes dehydration of the micelles and lowering of zeta potential at the interface, that of the transition metal cations brings about complex formation with ionic groups of proteins (ionizing at *p*H 11 or 7·5 as the case may be) yielding the insoluble products. Such a phenomenon has been observed by other workers[8,9] also who followed the equilibrium dialysis technique in the case of bovine serum albumin, pepsin and α-casein. The concentration of the monovalent Ag^+ ion required for this purpose was expectedly higher than that of the remaining bivalent transition metal cations included in Table 1.

The flocculation values of sodium and potassium salts for the various protein sols stabilized in the acid range ($pH = 2·5$) at which the particles carry positive charge, are given in Table 2. The valency rule, evidently, is not valid in these cases since SO_4^{2-} ion is seen to be a much weaker flocculent than either $Cr_2O_7^{2-}$ or HPO_4^{2-} ion, although all the three ions are divalent. Similarly, the trivalent AsO_3^{3-} ion is seen to be a weaker flocculent than the trivalent $[Fe(CN)_6]^{3-}$ ion. This anomalous behaviour of the anions may be traced, amongst other things, to the adsorbability by colloidal particles, which increases with the increase in size of the ion.

It is seen that amongst the two varieties of soybean proteins, the Bragg variety forms a relatively more stable sol than the Punjab variety at either *p*H. Further, the glycinin fraction of each soybean protein as well as arachin and conarachin fractions of peanut protein yield relatively more stable sols than the whole unfractionated proteins. The reason for this may lie, in part at least, in the fact that while NaOH was used for the extraction of whole proteins, NaCl was used for the extraction of the fractions from the same source[6]. It has been pointed out earlier[6] that the hydrocarbon chain in proteins isolated using salt solutions is coiled up to a larger extent. Such molecules, evidently, are less exposed to the action of added electrolytes and, therefore, give more stable colloidal systems.

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Salt Effects in the Solvolysis of Some Alkyl Chlorides in Different Solvent Systems

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The effect of different salts on the rates of solvolysis of *t*-butyl, *t*-pentyl, dimethylethylcarbinyl, and triethylcarbinyl chlorides has been studied in aq. DMSO, aq. acetone and aq. ethanol. Generally, the pattern of results show increased salt effect in the order NaCl < $NaNO_3$ < $LiClO_4$. For the first two salts, the effect decreases as the series is ascended, and for the last, the reverse trend is obtained. Discussion is largely based on the interplay of two factors, viz. effect on the stability of the initial state and solvent structure-induced ion pairing.

SALT effects on the rates of S_N1 reactions have been discussed by several workers[1-6], and it is clear that the Hughes-Ingold method of applying the Debye-Hückel theory is an over-simplification[7]. The factors which have to be taken into consideration are: (i) effect on the initial and transition states, and (ii) salt-solvent interactions. Because of the simultaneous operation of several of these factors, it has not been possible to assess their relative importance under various situations. One approach to the problem, which we have adopted here, is to study the effect of various electrolytes in different solvent systems, on substrates which have close structural similarities.

The alkyl chlorides were prepared by the standard methods[8]. The procedure adopted has been described earlier[9]. The variation in the values of the rate constants between replicate runs did not exceed 2%.

The kinetic data on the solvolysis of *t*-butyl, *t*-pentyl, diethylmethylcarbinyl, and triethylcarbinyl chlorides in the presence and absence of electrolytes are given in Tables 1 and 2. Data in 80% aq. DMSO have already been reported[10], which have been discussed on the basis that there is no selective ion solvation[11]. In 90% aq. DMSO, the percentage increase in the rate were as follows (65°): *t*-butyl: $0{\cdot}1M$ NaCl, +16·1; $0{\cdot}1M$ $LiClO_4$, +8·8; Et_3CCl: $0{\cdot}1M$ NaCl, +23·4; $0{\cdot}1M$ $LiClO_4$, +11·3. The ionic atmosphere effect should be larger for *t*-butyl chloride[8]. It is known, however, that dipolar aprotic solvents can solvate polarizable transition states of both S_N2[12], and S_N1[13] reactions, and further that anion solvation increases with polarizability[12]. It follows that solvation by DMSO will be greater for the transition state of triethylcarbinyl chloride in the presence of perchlorate ion. A combination of these two factors can account for the results.

In 50% aq. acetone, the concentration dependence of the rate in the presence of NaCl and $NaNO_3$ is not linear while for $LiClO_4$ there is a linear relationship. The linear relationship can be explained by assuming solvent structure-induced ion pairing effect[4]. The results with NaCl and $NaNO_3$ can be attributed to a salt-induced medium effect. The data in 60% aq. acetone can be accounted for as follows. Because of the preferential solvation of chloride ions by water, it is likely that the alkyl chloride will be salted into acetone. This effect should increase with the size of the alkyl chloride. Such salting-in has been observed earlier[14]. The salting-in effect of nitrate is less than that of chloride[3], and so this salt shows larger rate increases. The effect of $LiClO_4$ is ascribed to solvent structure-induced ion pairing effect. The data in 80% aq. acetone can be accounted for similarly.

In 90% aq. acetone, the percentage increase in rate in the presence of $0{\cdot}1M$ NaBr and $0{\cdot}1M$ $LiClO_4$

TABLE 1 — EFFECT OF ADDED ELECTROLYTES ON THE RATE OF SOLVOLYSIS OF ALKYL CHLORIDE ON AQ. ACETONE

Alkyl chlorides ($0{\cdot}05M$)	10^4k_1 (sec^{-1})	% of k_1 in the presence of					
		NaCl		$NaNO_3$		$LiClO_4$	
	(normal)	$0{\cdot}05M$	$0{\cdot}1M$	$0{\cdot}05M$	$0{\cdot}1M$	$0{\cdot}05M$	$0{\cdot}1M$
		50% AQ. ACETONE (20°C)					
Me_3CCl	1·29	+3·1	+4·7	+5·4	+7·0	+5·4	+10·9
		60% AQ. ACETONE (35°C)					
Me_3CCl	1·80	+5·0	+6·7	+10·0	+12·2	+10·6	+16·7
Me_2EtCCl	2·71	+4·4	4·4	+6·3	+9·2	+10·0	+16·6
Et_2MeCCl	3·79	+2·4	+1·6	+6·9	+8·7	+10·8	+18·7
Et_3CCl	3·94	−0·3	−2·5	+5·6	+7·9	+11·4	+18·6
		80% AQ. ACETONE (58°C)					
Me_3CCl	0·850	+15·3	+22·4	+12·6	+23·5	+15·7	+27·1
Me_2EtCCl	1·17	+11·1	+19·7	+11·1	+19·7	+14·5	+28·2
$EtMe_2CCl$	1·65	+10·3	+10·3	+9·1	+15·2	+13·9	+27·9
Et_3CCl	1·72	+5·2	+3·5	+7·6	+16·3	+14·5	+28·5