

the yields in the two cases. These results suggest that depending on the relative concentration of O_2 and I_2 in the system, they compete as scavengers for the cyclohexyl radical.

Photolysis of aerated cyclohexane with the 2537 Å radiation produced a product which was identified as organic peroxide from its unique reaction with KI (ref. 8). The estimated quantum yield for the peroxide formation was 1.3. The quantum yield of H_2O_2 was less than 0.05 in the system. Deaerated cyclohexane or deaerated I_2 -cyclohexane solution on photolysis did not show the peroxide reaction. Whether the mechanism of peroxide formation involves the production of a cyclohexyl radical as the primary step followed by cyclohexyl, oxygen addition and conversion to the peroxide or a rearrangement of the O_2 - C_6H_{12} complex under photolytic excitation to give the peroxide $C_6H_{11}O_2H$ is not clear. That the reaction involving cyclohexane solvent is unique due to the presence of CT band is underscored by the observation that whereas I_2 in benzene on photolysis with 2537 Å light (CT band λ_{max} at 295 nm) produced iodobenzene, no peroxide was formed on photolysis of aerated benzene.

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Apparent Molar Volumes of Some Common Salts in Water-N-Methylacetamide Mixtures of Varying Dielectric Constants

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The nature of the slope S_v of the empirical Masson's equation, $\varphi_v = \varphi_0 + S_v \sqrt{C}$ for some common salts NaBr, NaCl, KBr, KNO_3 and NH_4Br has been examined in water-N-methylacetamide mixtures of varying dielectric constant. Strong dependence of the nature of the slope (positive or negative) on the dielectric constant of the medium is indicated.

IN continuation of our earlier studies¹⁻³ on the dependence of the positive or negative nature of the slopes (S_v) of the ϕ_v vs $\sqrt{C}$ curves on the dielectric constant of the medium, the work has

now been extended to mixtures of water and N-methylacetamide (NMA). Although a negative slope is a general feature of the tetraalkylammonium salts (R_4NX) in solvents of high dielectric constants, it is only in NMA⁴ and N-methylpropionamide^{5,6} (NMP) that some common salts, containing small compact ions, give a negative slope⁷. It has already been reported that the negative slope for the R_4NX salts in water changes to a positive one when the dielectric constant of water is reduced by adding appropriate quantities of a solvent of lower dielectric constant like methanol¹, dioxane², and ethanol³. It would be instructive to investigate how the negative slope, observed for some common salts in NMA would change on reducing the dielectric constant of the solvent by adding suitable quantities of water in which the same salts have a positive slope. This aspect forms the subject matter of this note.

N-Methylacetamide (Fluka, purum) was fractionally crystallized and kept overnight on freshly ignited quicklime. It was then distilled under reduced pressure and the middle fraction collected. The process of purification was repeated with the middle fraction until the electrical conductance of the sample was of the order of 10^{-6} mho or less. The salt samples (AR, BDH), were recrystallized from conductivity water. Solutions were prepared on molal basis and the density of solutions determined as described earlier¹. From the density data thus obtained, apparent molar volume ϕ_v was calculated in the usual manner and the ϕ_v vs $\sqrt{C}$ curves were drawn for different electrolytes*.

Since the ϕ_v vs $\sqrt{C}$ curves are almost linear for all the salts employed Masson's equation (1),

$$\phi_v = \phi_0 + S_v \sqrt{C} \quad \dots(1)$$

would be applicable in all the cases. It may be noted that the slope is positive for mixtures containing 0.0, 10, 20, 40 and 50% NMA but it is negative for 60% and 100% NMA (Table 1). Estimated dielectric constants of the former are 78, 87, 99, 118 and 127 and of the latter 138 and 178 respectively (Table 1). These values indicate that a high dielectric constant favours a negative slope while a smaller one a positive slope. It is also observed that the ϕ_v is large and the slope small when the

TABLE 1 — SLOPE S_v FOR SOME COMMON SALTS IN DIFFERENT WATER-NMA MIXTURES

Wt % NMA in the mixture	Dielec- tric con- stant	$S_v \times 10^{-1}$ at 35° for				
		NaCl	NaBr	KBr	KNO_3	NH_4Br
0 (water)	78	200	154	214	208	210
10	87*	172	125	182	125	162
20	99*	138	116	166	100	133
40	118*	100	80	110	80	120
50	127*	77	74	83	72	94
60	138*	-15	-25	-30	-36	-27
100 (NMA)	178	-24	-30	-50	-41	-55

*Estimated values assuming linear relation between % composition and dielectric constant of the mixture.

*Authors may be contacted for detailed data.

dielectric constant of the medium is high. The negative slope for these salts in pure NMA becomes positive when the dielectric constant of the solvent is reduced by adding water. It may be remembered that the negative slope in the ϕ_0 vs $\sqrt{C}$ curves for the salts containing the larger R_4N^+ ions in water was explained as due to the alkyl chain-water interaction (hydrophobic) by Wen and Saito⁸. Similar negative slope for these salts in non-aqueous solvents of high dielectric constant like formamide^{9,10}, N-methylacetamide⁴, N-methylpropionamide⁵ and ethylene carbonate¹¹ was explained as due to cation-cation and cation-anion penetrations at the higher concentrations. A lyophobic alkyl chain-solvent interaction, as in water, is not likely to occur in these non-aqueous solvents; also interionic penetration is not possible in the case of salts containing small compact ions like Na^+ , K^+ , NH_4^+ , Br^- and NO_3^- . Hence some other factors must be responsible for the negative slope for the salts like NaCl, NaBr, KBr, KNO_3 and NH_4Br in NMA and some other similar cases in NMP.

A reference to the already available data in different solvents, including water, leads one to conclude that, in general, negative slope is favoured (i) if the dielectric constant of the medium is high, whether the solvent is hydrogen bonded like formamide, NMA and NMP or non-hydrogen bonded like ethylene carbonate and (ii) if the electrostatic ion-ion interaction is weak due to large ionic size as for R_4N^+ ions or due to the very high dielectric constant as in NMA and NMP in which negative slope is reported both for the R_4NX and some common salts used in this investigation. On the other hand, a positive slope is favoured by strong electrostatic ion-ion interaction due to the low dielectric constant of the medium. These results lead one to conclude that, in general, dielectric constant of the medium is mainly responsible for the nature of the slope of the ϕ_0 vs $\sqrt{C}$ curves. The behaviour of the larger R_4NX salts in water (i.e. the negative slope in their ϕ_0 vs $\sqrt{C}$ curves) can also be explained on this ground without invoking Frank's hypothesis of the water repelling effect of the alkyl chains of the R_4N^+ ions and the resulting water-structure enforcement as has been done by some workers⁸.

However, besides the dielectric constant, some other factors also appear to play a role in influencing the nature of the slope. For example, Me_4NX and Et_4NX salts have a positive slope in NMA and NMP and even in water (Et_4NX is a border-line case in this solvent) although Me_4N^+ and Et_4N^+ are large ions as compared to Na^+ , K^+ , Cl^- and Br^- etc., the salts like NaCl, NaBr, KBr, KNO_3 give a negative slope in NMA. Several other anomalies, which cannot be explained on dielectric constant concept, can also be pointed out; for example, in the case of HCl, where both the ions are smaller in size give a negative slope in formic acid medium of comparatively small dielectric constant ($\epsilon_{16} = 58$). However, both the conditions should favour a positive slope. Hence it is clear that other factors, besides the dielectric constant of the medium, appear to play a role in controlling the nature of the slope. A wider and planned study of the problem is very

much called for in order to arrive at a satisfactory solution.

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Binary Oxide Systems, MnO-ZnO & MnO-CdO*

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Solid solutions of zinc oxide in manganous oxide have been prepared below 800°. These are stable in air and X-ray powder patterns and chemical properties confirm the formation of solid solutions up to 10 mole % of ZnO in the MnO. Cadmium oxide, however, seems to dissolve very little in MnO.

SOLID solutions of metallic oxides in one another are of both fundamental and applied interest. Particularly interesting is the stabilization of unstable and oxygen-sensitive oxides such as ferrous and manganous oxides by dissolving in them even small amounts of other oxides.

Koltashkina *et al.*¹ have prepared solid solutions of zinc oxide in manganous oxide at 1200°, while the CdO-MnO system has not been studied so far. It is the object of the present investigation to study the latter system and also to prepare these systems at much lower temperatures which are preferable to avoid volatilization of zinc and cadmium oxides. Also their value as catalyst materials is increased thereby since the oxides are liable to sinter and lose their activity at too high temperatures. We have also attempted a more detailed study of the MnO-ZnO system than that reported hitherto.

The MnO-ZnO samples were prepared by carefully heating up to 700° appropriate mixtures of precipitated manganous and zinc oxalates out of contact

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