

Ponderal Substituent Effect on the Solubility of an Octahedral Metal Complex and its Quantitative Correlation

J.M. JESSY

*Department of Chemistry, University of Calicut
Calicut-673 635 (Kerala), India*

Solubilities of the cobalt(III) complex, $\text{Co}[(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ were determined in alcohol-water mixtures of lower aliphatic alcohols. The solubility was found to decrease steadily with increasing alkyl substitution in the alcohol. This is attributed to the ponderal effect of the alkyl groups. As expected for ponderal effect, the logarithm of relative solubilities determined by two different methods gives good linear correlation with $\log(1/\mu)$ where ' μ ' is the reduced molecular weight of solvent and solute.

INTRODUCTION

The ponderal effect due to the changing of alkyl substitution in solvent has been demonstrated for various systems in alcoholic and aq. alcoholic solvents.¹ Alcohols of the α -series (methanol, ethanol, isopropanol and tertbutanol) and of the normal series (ethanol, *n*-propanol, *n*-butanol . . . *n*-decanol) had been used, their choice being in view of all of them having nearly the same polarity (dipole moments within the range of 1.63 D to 1.81 D); the reaction systems had been so chosen that the reactivities were determined by degree of solvation. In all the systems, the logarithms of the reactivity parameters had been demonstrated to be giving very good linear correlation with the function $\log(1/\mu)$ where ' μ ' is the reduced molecular weight of the solute and the solvent. A mathematical relationship had been derived, justifying the linear correlations (obtained earlier as empirical relationships) as a consequence of ponderal (or mass) effect of the alkyl substituents on the solvation bonds.

The present work was aimed at testing the relationship further. The process selected is the dissolution of the metal complex, $\text{Co}[(\text{NH}_3)\text{Cl}]\text{Cl}_2$, in the same two series of alcohols mentioned above with the degree of solvation expected to be the determining factor for the extent of dissolution. The particular complex was chosen as one of the well-studied² complexes whose structure, geometry, method of preparation, properties etc. are known. Also the doubly charged cation that the metal forms in solution must favour greater solvation, which might be significant in view of the steric hindrance possible for solvation due to the ligands. The solubility of the complex in each alcoholic solvent should be a measure of its degree of solvation in that solvent, with other conditions remaining constant.

EXPERIMENTAL

The complex, cobalt monochloropentammine chloride, was prepared and purified, and the alcohols were purified by standard methods³. The identity of the purple-coloured complex prepared was confirmed by gravimetric estimation of cobalt in the oxide Co_2O_3 obtained by heating the complex strongly in air.

Solubility determinations were made not in pure alcohols but in alcohol-water mixtures, as the complex was not sufficiently soluble in the alcohols. This is justified on the basis that the effect of alkyl substitution in solvent and its quantitative correlation with the reduced molecular weight function were observable in aqueous alcohols as well as in pure alcohols if the molar percentage of water is kept constant in all the alcohol-water mixtures, which keeps the selective solvation by water and its effect on reactivity constant.⁴ Even though effort was made to keep the water-content in the mixtures at minimum, it was necessary to have the solvents prepared with alcohol to water ratio at 1 : 6 mole/mole, for all the alcohols of the α -series.

Solubilities in these aqueous alcohols were compared in two ways.

(a) Gravimetric method: Solvent mixtures in the above ratio were prepared and stored in tightly stoppered bottles with little air space to avoid relative evaporation of the alcohol. A saturated solution was prepared in a 200 mL glass-stoppered conical flask using about 150 mL solvent and excess complex. The flask was placed in a thermostated bath (Toshniwal-GL 15) kept at $40 \pm 1^\circ\text{C}$ for 30 min with shaking every 5 min. The contents were then allowed to settle for 10 min. (in the water bath). 100 mL of the supernatant saturated solution was carefully pipetted into a weighed crucible. The solvent was allowed to evaporate by slow heating at first and then, when all the solvent was evaporated, the residue was heated strongly, in air, to convert the complex to its oxide completely. [This conversion to oxide was because drying of the complex itself by heating was not possible due to its tendency for easy decomposition.] The crucible was cooled and weighed; heating and cooling were repeated until the weight remained constant. From the weight of the oxide, Co_2O_3 , the weight of the complex $\text{Co}[(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in saturated solution at 40°C was calculated. The process was done in triplicate for solvent mixtures of each alcohol. The average of the triplicate values (which showed a variation of less than 8% overall) was taken for each solvent.

(b) Spectroscopic method: Solvent mixtures were prepared and stored as before. The instrument used was UV-visible spectrophotometer, Shimadzu 1049. As its cell compartment was not separately thermostated, the temperature of the air-conditioned 10 ft. \times 8 ft. room in which the spectrophotometer was kept and which was maintained at 28°C , was taken as the suitable temperature, taking care to keep the door closed throughout the experiment. Saturated solutions were prepared as before, with excess complex in solvent mixtures. The solutions in conical flasks were placed in a water bath kept in the room for 12 h. The temperature of the bath remained constant at $28 \pm 1^\circ\text{C}$. Each solution was allowed to stand in the water bath for 30 min with shaking every 5 min (to help precipitate excess solute from the saturated solution prepared outside the room, at 32°C) and

then the solute was allowed 10 min. to settle. The supernatant saturated solution was pipetted into the sample cell; the corresponding aqueous alcoholic solvent was pipetted into the blank cell. The absorbances were determined at two wavelengths: $\lambda = 534$ nm and $\lambda = 364$ nm, at which absorption maxima had been observed for the complex in water solution in an earlier experiment.* The process was done in triplicate for solvent mixtures of each alcohol and the average value taken; variations within the triplicate values were less than 5%.

In the case of alcohols of the normal series there was the additional problem of lack of miscibility with water. This could be overcome somewhat by introducing a third component in the solvent system—the non-complexing acetone—and keeping its molar concentration constant for all the alcoholic solutions. However the alcoholic content of the solvent system had to be—after a number of trials—so low (at about 0.4 molar per cent) that one could not be sure that any solvent effect was due to the alcohol, not to mention its substituent. Therefore determination of relative solubility of the complex in normal series by this method had to be given up. The absorbances which were nevertheless measured did not show any regular gradation.

RESULTS AND DISCUSSION

Results of the experiments described above are given in Tables 1 and 2 for alcohols of α -series along with the calculated parameters required for quantitative correlation-logarithm of solubility S [$\log S$] from the gravimetric method and the logarithm of absorbance A [$\log A$] from the spectrophotometric method, both of which are the reactivity parameters for the process of dissolution of the complex (which depend on degree of solvation). The tables also give values of $\log(1/\mu)$ for the different alcohols, which is the parameter with which linear correlation is

expected for ponderal effect (μ being given by $\mu = \frac{M_1 M_2}{M_1 + M_2}$ where M_1 is the mol. wt. of the complex and M_2 , that of the alcohol in the solvent). Also included are the values of the steric substituent constant, E_s , of the different alkyl substituents in the alcohols, with which linear correlation is expected for steric effect.

Substituent effects—inductive, mesomeric, steric and related effects—first established in organic reactions, have been recognized in inorganic systems also. It is only reasonable therefore that ponderal effect also be looked for in inorganic systems.

The substrate used (as solute), cobalt monochlorammine chloride, ionizes into the complex ion, $[\text{Co}(\text{NH}_3)\text{Cl}]^{2+}$ and Cl^- . In the aqueous alcoholic solvents used, with 85% (molar) of water, it must be completely ionized and, at concentrations of the order of only 10^{-3} moles per litre at saturation point, completely solvated. The complex ion being so much larger and with all the ligands around, the *solvation of this ion* (rather than that of the smaller, easily hydrogen-bonded chloride) must be the limiting and therefore *determining factor for solubility* of the salt in the aqueous alcohols.

*These are the absorptions due to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions.

TABLE-1
MOLAR SOLUBILITIES OF $\text{Co}[(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ IN aq. ALCOHOLS OF THE α -SERIES
AND THEIR CORRELATIONS WITH MASS FUNCTION μ

Alcoholic component in solvent	Wt. of Co_2O_3 (g)	Wt of complex in 100 mL (sat. soln.) (g)	Solubility of complex, S (moles, $\text{lit}^{-1} \times 10^3$)	$\log S + 3$	Mass function $1/\mu \times 10^2$	$\log (1/\mu) + 2$	E_s^5 values of alkyl substituents
MeOH	0.0718	0.2240	8.90	0.949	3.521	0.547	0
EtOH	0.0432	0.1348	5.38	0.731	2.571	0.410	-0.07
<i>i</i> -PrOH	0.0350	0.1092	4.36	0.640	2.064	0.315	-0.47
<i>t</i> -BuOH	0.0262	0.0818	3.26	0.514	1.749	0.243	-1.54

Correlation coefficient (r): $\log S$ vs. $\log (1/\mu)$: $r = 0.996$

TABLE-2
ABSORBANCES DUE TO Co(III) IN SATURATED SOLUTIONS OF THE COMPLEX
IN AQUEOUS ALCOHOLS OF THE α -SERIES AND THEIR CORRELATION WITH
MASS FUNCTION μ

Alcoholic component in solvent	Absorbance (A)		Logarithm of Absorbance ($\log A + 1$)		$\log (1/\mu) + 2$	E_s^5
	$\lambda = 534$	$\lambda = 364$	$\lambda = 534$	$\lambda = 364$		
MeOH	0.525	0.499	0.7202	0.6981	0.5467	0
EtOH	0.282	0.267	0.4502	0.4265	0.4101	-0.07
<i>i</i> -PrOH	0.191	0.181	0.2810	0.2577	0.3147	-0.47
<i>t</i> -BuOH	0.140	0.133	0.1461	0.1239	0.2428	-1.54

Correlation coefficient (r): $\log (A)$ vs. $\log (1/\mu)$: λ_{534} $r = 0.999$, λ_{364} $r = 0.999$

The complex ion is believed to have its six 3d-electrons in its t_{2g} orbitals and to have its two e_g orbitals hybridized with 4s and 4p orbitals to give six d^2sp^3 orbitals which are filled by its ligand electrons.* Therefore the next available vacant orbitals are the 4d orbitals. In solvating the complex ion, the oxygen of any water or alcohol molecule will have to have its non-bonding electrons interact with the 4d orbitals. This can happen only with the formation of *solvation bonds of the 'd $_{\pi}$ -p $_{\pi}$ ' type*. Such ' π -model' solvation bonds must be weaker than the σ model solvation bonds one often encounters in the carbonium-ion solvation in organic reactions. This, coupled with the size of the complex ion which must keep

*Organic chemist-reader may be reminded: In $\text{Co}[(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, cobalt has an electrovalency of +3, by having transferred to three chlorine atoms one electron from its 3d orbitals and two from its 4s orbital. The six remaining electrons fill the degenerate non-bonding t_{2g} orbitals, d_{xy} , d_{yz} and d_{xz} . The slightly higher-energy, degenerate e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) hybridize with 4s and 4p to give d^2sp^3 -hybridized orbitals which are empty and directed towards the corners of an octahedron; these are filled by the non-bonded electrons of the six ligands. One of the chloride ions plays the additional role of a ligand, and, in the process, neutralizes one of the charges created on the cobalt (Co^{3+}) due to ionization. The complex ion is therefore only doubly charged and electrovalently bonded to two Cl^- ions outside the coordination sphere.

the solvating molecule at a greater distance from the charged nucleus, can account for the *low solubility of this salt in the solvents used. Nevertheless the role of the alcohol in solvating the ion is indicated* by the observation that when molar percentage of water is kept constant, the solubility changes with changing of the alcohol in the solvent even with the molar content of alcohol only about 15% in the solvent, while that of water is 85%.

The additional observation is that the solubility changes are caused not by changing the (molar) percentage of alcohol in the solvent, but by changing the number of alkyl groups on the central carbon of the alcohol. Therefore alkyl groups, in spite of their very minor position as substituents in the solvent—rather in the minor component of the mixed solvent—*do produce a strong-enough substituent effect to change the solubility* of this weakly soluble salt by about three times in going from methanol to tert.-butanol.

It need to be remembered that the primary interaction between the cationic solute and the alcohol is the formation of the solvation bond by virtue of the dipolar nature of the alcohol. This may be referred to as the solute-solvent interaction at the macroscopic level.¹ *What the substituents contribute are effects at the microscopic or molecular level in determining the strength of this solvation bond.*

Alkyl substituents can produce polar, steric and, as described in the earlier work, ponderal effect. The polar effect, mesomeric in character mainly, is to release electron density to alcoholic oxygen which must increase solvation and therefore solubility. The steric and ponderal effects—which could be large as the complex ion is bulky and massive—must be solvation-hindering and therefore negative. The observation, that solubility steadily decreases with increasing alkyl substitution, indicates that the predominant effect must be one or both of the latter, and *not polar* effect.

To distinguish between the steric and ponderal effects a correlation was attempted, first between relative solubility and Tafts' steric substituent constant, E_s . As E_s is defined in terms of logarithm of reactivity parameter in the absence (or constancy) of polar effect by a linear free-energy relationship [$\log(k/k_0) = E_s$], a linear correlation was looked for between the logarithm of the solubility parameter ($\log S$) and E_s values of the corresponding alkyl substituents and also between the logarithms of the absorbances (which are parameters of relative solubility), $\log(A)$ values, at $\lambda = 534 \text{ nm}$ and $\lambda = 354 \text{ nm}$ and the same E_s values. No such correlation was however obtained; *cf.* Figs. 1 and 2 and correlation coefficients in

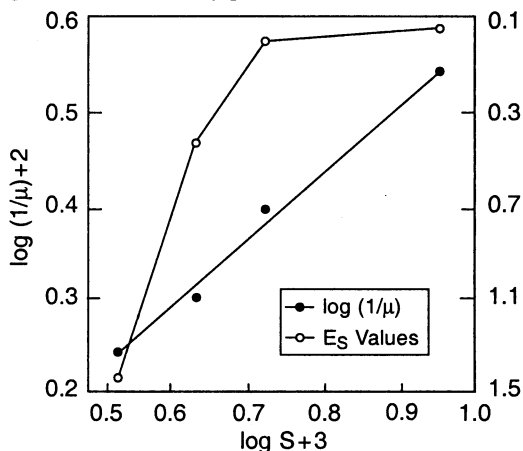


Fig. 1. Plot of $\log S$ vs. $\log(1 + \mu)$ and vs. E_s

Tables 1 and 2. This leads to the inference that substituent effect produced is not steric.

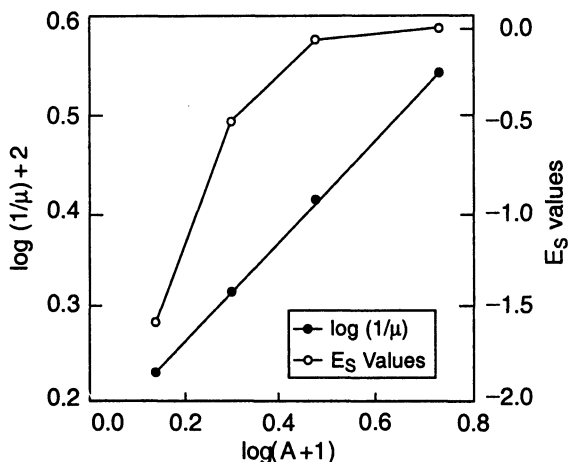


Fig. 2. Plot of log A vs. log (1/μ) and vs. E

Next, correlations were attempted for these parameters of solubility namely log (S) and log (A) (the latter at the two wavelengths as above) against the mass function log (1/μ). A linear correlation was again looked for, since such correlation has been reported earlier for ponderal effect¹. A good linear correlations have been obtained as shown in Figs. 1 and 2 (only one plot of log A vs. log (1/μ) (at λ = 534 nm), is given, the other (at λ = 354 nm) being very similar); and as indicated by the values of correlation coefficient (0.998, 0.999 and 0.999 respectively) as given with the Tables 1 and 2. This is taken as confirmation that the alkyl substituent effect is ponderal.

Conclusion

Ponderal effect due to alkyl substituents in solvent is demonstrated for solutions of an inorganic complex salt in alcoholic solvents in spite of very low solubility.

REFERENCES

1. J.M. Jessy, *Asian J. Chem.*, **12**, 145 (2000).
2. F. Basolo and R.G. Pearson, *Mechanism of Inorganic Reactions : A Study of Metal Complexes in Solution*, 2nd Edn., J. Wiley & Sons, Inc., London (1967) and other texts.
3. A.I. Vogel, *A Text Book of Practical Organic Chemistry*, Longmans, London, p. 276 (1956).
4. J.M. Jessy, *Curr. Sci. (India)*, **53**, 1025 (1984).
5. M.S. Newman (Ed.), *Steric Effects in Organic Chemistry*, J. Wiley & Sons, Inc., New York, p. 601 (1956).