

Phase transitions in metal perchlorate hydrates: The supposed hydrate-to-pseudohydrate transformations

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However, only for higher values of ρ ($\rho = 0.3, 0.5$) did the data for the available values of l appear to have converged to the $l \rightarrow \infty$ limit.

The data of Okamoto¹ are plotted in Fig. 1 in order to test Eqs. (3) and (4). The results give fairly strong evidence for Eq. (3) but it is impossible to assess consistency or inconsistency with Eq. (4) because no error bars are reported.

In order to fully test the scaling laws, Eqs. (1)–(4), more evidence (with error bars) is needed in the two regimes which are insufficiently covered by the available data: (a) ρ small, l very large (b) ρ large, l moderately large.

I wish to thank Alan Sokal for helpful discussions.

¹H. Okamoto, *J. Chem. Phys.* **79**, 3976 (1983).

²M. Daoud, J. P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, and P. G. deGennes, *Macromolecules* **8**, 804 (1975).

³P. G. deGennes, *Isr. J. Chem.* **14**, 154 (1975); *J. Polym. Sci. Polym. Lett.* **15**, 623 (1977).

⁴S. G. Whittington, *Adv. Chem. Phys.* **51**, 1 (1982).

⁵M. Bishop, M. H. Kalos, A. D. Sokal, and H. L. Frisch, *J. Chem. Phys.* **79**, 3496 (1983).

⁶Recent light scattering experiments have demonstrated a similar scaling law for the static screening length, as well as the universality of the corresponding scaling function. See P. Wiltzius, H. R. Haller, D. S. Carmel, and D. W. Schaefer, *Phys. Rev. Lett.* **51**, 1183 (1983).

⁷H. Okamoto, K. Itoh, and T. Araki, *J. Chem. Phys.* **78**, 975 (1983).

⁸F. T. Wall, J. C. Chin, and F. Mandel, *J. Chem. Phys.* **66**, 3143 (1977).

⁹E. deVos and A. Bellemans, *Macromolecules* **7**, 812 (1974).

Phase transitions in metal perchlorate hydrates: The supposed hydrate-to-pseudohydrate transformations^{a)}

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Patel and Bist recently^{1,2} reported that cooling produced an abrupt change in the infrared spectrum of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. They have since reported similar changes in the spectra of $\text{Hg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and have interpreted these changes as being caused by phase transitions involving transformations of these salt hydrates to *pseudohydrates*, i.e., structures consisting of H_3O^+ and OH^- ions instead of water molecules.^{3,4} Pseudohydrates are of common occurrence, but Patel and Bist's suggestion that a normal hydrate transforms to a pseudohydrate *on cooling* is unusual and surprising.

The major spectral changes observed by Patel and Bist were: (i) replacement of the OH stretching fundamental of water by a strong absorption centered at 3220 cm^{-1} , with shoulders at 3365 and 3125 cm^{-1} ; (ii) a broadening and weakening of the H_2O bending fundamental at about 1650 cm^{-1} ,²⁻⁴ described in Ref. 2 as a "hypochromic effect"; and (iii) appearance of a new, broad, and intense absorption band at 850 cm^{-1} , in the region of H_2O librations.³

We believe that the explanation of Patel and Bist is incorrect and that these spectral changes were in fact due to the crystallization of excess moisture adhering to their samples. As the authors themselves point out, the perchlorate hexahydrates are very hygroscopic, so that even a previously dry material will rapidly take up a large amount of moisture during sample transfers and during the required grinding. Any moisture in the sample may then react with the alkali halide windows used to contain it.^{3,4} Lowering the temperature may therefore bring about (1) crystallization of ice, (2)

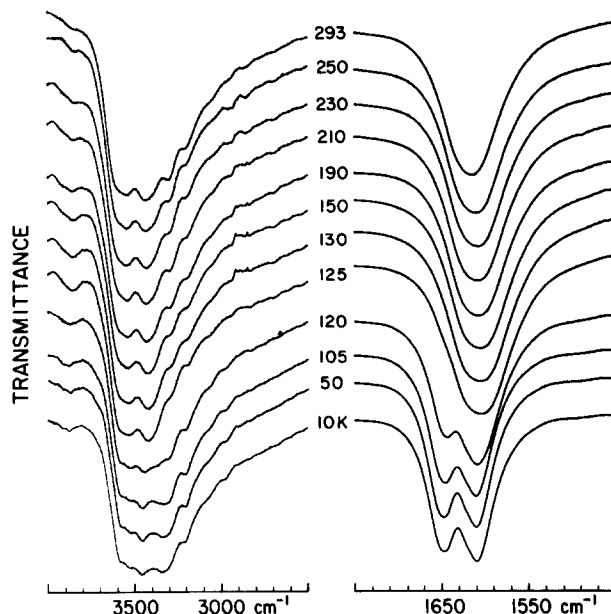


FIG. 1. Infrared spectra of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ at different temperatures in the region of OH stretching (left) and H_2O bending (right). The spectra were recorded on a Fourier-transform IR spectrometer (Bomem DA3.02) fitted with a closed-cycle He refrigerator. Samples were prepared by the aqueous reaction of stoichiometric quantities of perchloric acid and cadmium carbonate. The product was twice recrystallized from water, filtered and stored in a desiccator over H_2SO_4 . Fluorocarbon mulls were prepared under a flow of dry nitrogen and were sandwiched between calcium fluoride windows. The mulls were dried overnight at 0.01 Torr within the cryostat prior to low-temperature spectroscopy.

crystallization of various hydrates depending on the salt windows used and the extent of ion exchange between the window material and the sample, and (3) formation of crystalline hydrates of perchloric acid, if traces of HClO_4 are also present.⁶

The temperatures at which such crystallizations might be expected to occur upon cooling are somewhat below 273 K, and this is where Patel and Bist observed the sharp spectral changes: at 256 K for the Zn salt,¹ at 243 K for the Hg salt,³ and at 248 K for the Cd salt.⁴ The major spectral features (i), (ii) and (iii) are characteristic of ordinary ice⁵ and clearly indicate ice formation. The additional small bands which were observed at 3595 and 1605 cm^{-1} in the low-temperature spectrum of the Hg salt,³ and at 3625 and 1579 cm^{-1} in the spectrum of the Cd salt,⁴ appear to be due to crystalline hydrates which we are unable to identify.

In order to settle the matter, we have examined the temperature variation of the infrared spectra of samples of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ of different degrees of dryness. Samples which had not been thoroughly dried produced spectra similar to those of Ref. 4, with prominent ice bands, and with additional spectral features when the samples had been sand-

wiched between alkali halide windows. In contrast, the spectra of dry samples showed no such changes upon cooling (Fig. 1) and varied slowly and gradually in the vicinity of 248 K, the reported temperature of the phase transition.⁴ Phase transitions were indeed observed at other temperatures; they clearly do not correspond to the formation of a pseudohydrate. We conclude that the supposed hydrate-to-pseudohydrate transformations^{3,4} and hypochromic effect,² reported by Patel and Bist, are artifacts of incomplete drying of their samples. A more detailed account of our calorimetric and spectroscopic studies of phase changes in perchlorate hexahydrates will be presented elsewhere.

^{a)}NRCC No. 23605.

¹M. B. Patel and H. D. Bist, *J. Phys. Paris Colloq.* **6**, 917 (1981).

²M. B. Patel and H. D. Bist, *J. Chem. Phys.* **76**, 6445 (1982).

³M. B. Patel and H. D. Bist, *J. Chem. Phys.* **79**, 4489 (1983).

⁴M. B. Patel and H. D. Bist, *Solid State Commun.* **48**, 139 (1983).

⁵J. E. Bertie and E. Whalley, *J. Chem. Phys.* **40**, 1637 (1964).

⁶Perchlorate salts are prepared by the action of dilute perchloric acid on the corresponding carbonates (Refs. 1–4), and we have found that even thorough washing does not always remove the last traces of acid.

Reply to "Comment on 'Phase transitions in metal perchlorate hydrates: The supposed hydrate to pseudohydrate transformations' "

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The following comments to be made on the preceding comment¹ on our work on divalent metal perchlorate hexahydrates.^{2–5}

I. $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$, and Hg) are hygroscopic but they are not deliquescent in air at low humidities such as prevailing in winter.⁶ The crystals grown from aqueous solution at room temperature are well known to be hexahydrates from x-ray study⁶ and only such samples were used in IR^{2–5,7,8} and Raman^{4,7,9} studies in low humidity ($\sim 30\%$) atmosphere.

In the hexahydrates the water molecules are weakly bonded in the above mentioned salts, therefore vacuum drying of the samples (used by Falk *et al.*¹) may result in dehydration thus producing lower hydrates. In lower hydrates (i.e., less than $6\text{H}_2\text{O}$ molecules) one would not expect formation of pseudohydrate according to our proposed model (see Ref. 4, Sec. IV C) based on crystal structure⁶ for Cd and Hg salts. Even in hexahydrates of salts other than Cd and Hg, one would not expect formation of pseudohydrate according to our proposed model.⁴ In fact we also did not observe the formation of pseudohydrate in other salts except Cd and Hg salts.^{2–5,7–9} In the case of Zn salt^{2,3} we have ruled out the

possibility of pseudohydrate formation due to absence of bands for OH^- and oxonium ions unlike the cases of Cd^5 and Hg^4 salts.

II. Falk *et al.*¹ have suggested that our observed spectral changes are entirely due to the crystallization of adsorbed water and the prominent bands are the ice band. However, recently it was found from the thermal study¹⁰ in $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ that the amount of adsorbed water is almost negligible (0.3%). Moreover, our IR studies^{2–5,7} under similar experimental conditions show different types of spectral behavior for different cationic salts, which suggests that the spectral changes with temperature are not associated with the crystallization of adsorbed water.

III. It was suspected by Falk *et al.*¹ that another cause of spectral change might be due to formation of crystalline hydrates of perchloric acid, which they are unable to remove completely from their samples used for experimental studies.¹ However, in our multiple recrystallized samples (used for experimental studies) we do not expect traces of HClO_4 which is supported by the fact that only a single totally symmetric stretching mode of perchlorate ion in Raman spectra is observed,^{3,7,9} which is forbidden in IR for perfect T_d sym-