Heterogeneous inorganic systems
VI.* Effect of cations on the formation of hydrogen phosphites in saturated aqueous solution

M. EBERT

*Department of Inorganic Chemistry, Faculty of Natural Sciences,
Charles University, CS-128 40 Prague*

The effect of the cations Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} on the formation of hydrogen phosphites in saturated aqueous solution has been studied using solubility diagrams in ternary systems containing phosphite, phosphorous acid, and water. This influence has been evaluated employing the relationship between the effective polarization strength of the cations, considering the mode of their hydration, P_{ef}, and the composition of the saturated aqueous solution at invariant points of the solubility curve at the beginning of the hydrogen phosphite formation. The composition of the saturated solution has been expressed in terms of the ratio of the stoichiometric ratio of the phosphorous acid and phosphite amounts, R_{stoich}, and the real mole ratio of their amounts, R_{real}, $M = R_{stoich}/R_{real}$. It has been found that the relationship between the effective polarization strength and quantity M can be expressed for the studied set of cations by the equation

$$M = 1.01(10^5 \cdot P_{ef}/pm^{-2}) - 2.51$$

It follows from this dependence that the effective polarization influence of the cations under the given conditions favours the formation of hydrogen phosphites and increases the strength of their hydrogen bonding, as observed earlier in a study of the changes in the standard Gibbs energy for the corresponding phase reactions.

Используя диаграммы растворимости в тройных системах, содержащих фосфит, фосфористую кислоту и воду, изучено влияние катионов Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+} и Ba^{2+} на образование гидрофосфитов в насыщенном водном растворе. Это влияние было оценено, используя зависимость между эффективной поляризационной силой катионов, учитывающей способ их гидратации, P_{ef}, и составом насыщенного водного раствора в инвариантных точках кривой растворимости в начале образования гидрофосфитов. Состав насыщенного раствора выражен посредством отношения стехиометрического отношения количеств фосфористой кислоты и фос-

---

фита, R_{stoich}, к действительному молярному отношению, R_{real}, $M =$ $= R_{stoich}/R_{real}$. Обнаружено, что взаимосвязь между эффективной поляризационной силой и величиной M может быть выражена для изучаемого набора катионов с помощью уравнения

$$M = 1{,}01(10^5 \cdot P_{ef}/\text{пм}^{-2}) - 2{,}51$$

Из данного выражения следует, что эффективное поляризационное влияние катионов при данных условиях ведет к предпочтительному образованию гидрофосфитов и увеличению прочности их водородного связывания, как отмечалось ранее при изучении изменений стандартной энергии Гиббса для соответствующих фазовых реакций.

In a study of the solubility diagrams for ternary systems with phosphites, phosphorous acid, and water [1—19] it has been found that various types of hydrogen phosphites are formed and some of them are repeated with various metals. Some systems involve only a single type of hydrogen phosphite, *e.g.* for lithium, $LiH(HPO_3)$, other systems contain several hydrogen phosphites, *e.g.* for manganese, $MnH_2(HPO_3)_2 \cdot H_2O$, $Mn_3H_2(HPO_3)_4 \cdot 1.5H_2O$, $MnH_6(HPO_3)_4 \cdot H_2O$, and $Mn_2H_6(HPO_3)_5 \cdot 4H_2O$. Hydrogen phosphites with one hydrogen atom in the phosphorous acid, replaceable by a metal, corresponding to the charge unit on the cation occur most often. The systems have been studied under identical pressures and temperatures and thus the variability in the hydrogen phosphite types and their stability depend on the effect of the cations and on the composition of the studied system [20]. This paper deals with the most common type of hydrogen phosphite with the anion $H(HPO_3)^-$, in order to elucidate the effect of the cations Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} on its formation in saturated aqueous solution.

Dependence between the polarizing effect of the cations and the composition of a saturated aqueous solution at invariant points of solubility diagrams

Selection of the characteristic parameters

To compare the systems with different cations, a suitable state of the system, characteristic from the given point of view, had to be found. An analysis of the solubility diagram indicated that these conditions were met by the state of saturated solution at the invariant point of the solubility curve at which the studied type of hydrogen phosphite begins to be formed. The state of a solution is best characterized by its composition. For the study, the ratio of the amounts of phosphorous acid and the given phosphite, R_{real}, was selected and related to the stoichiometric ratio of these amounts, R_{stoich}. The quantity, characterizing

saturated solution at the given invariant point of the solubility curve, is thus the ratio of the stoichiometric ratio of the amounts of phosphorous acid and the phosphite and the real ratio of their amounts, $M = R_{stoich}/R_{real}$. The polarization strength of the cations, $P = q/r^2$, where q is the charge number of the cation and r is its radius according to Goldschmidt [21] (or *Yatsimirskii* [22] for NH_4^+), has been selected as the characteristic parameter of the cations.

Dependence of the composition of saturated aqueous solution,
expressed in terms of M, on the polarization strength of the cation, P

The experimental data for M have been taken from the works dealing with the formation of hydrogen phosphites and employing solubility diagrams for the appropriate systems with phosphites [1—9]. The dependence of the composition of saturated aqueous solution, M, on the cation polarization strength, P, is depicted in Fig. 1 and the appropriate values are given in Table 1. The unit
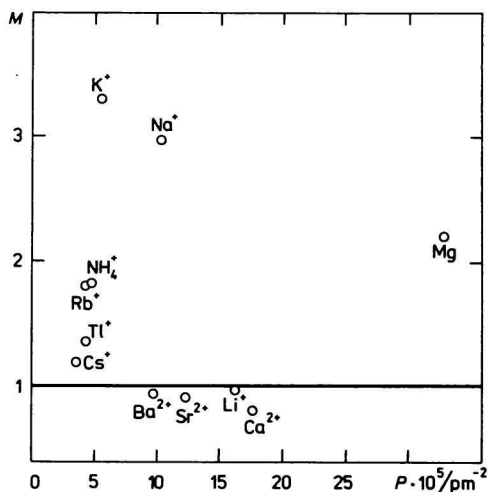

Fig. 1. Dependence of the ratio of the stoichiometric ratio of amounts of phosphorous acid and phosphite and the real ratio of their amounts, M, on the polarization strength of the cation, P, at invariant points of the solubility diagram for the beginning of the hydrogen phosphite formation.

value of M is marked in the figure, as the boundary between the phosphites that are congruently soluble in water and those soluble incongruently. The following conclusion can be drawn from the distribution of the points: 1. The smallest amount of phosphorous acid, H_3PO_3, required for the phase reaction with formation of hydrogen phosphite, is demanded by dipotassium phosphite, K_2HPO_3 and the largest amount by calcium phosphite. 2. A better stability of hydrogen phosphites is obtained in saturated aqueous solution in the presence of cations with a single charge than with doubly charged cations which yield, except for magnesium cation, Mg^{2+}, hydrogen phosphites that are incongruent-

Table 1

Dependence of the ratio of the stoichiometric ratio of the amounts of phosphorous acid and phosphite, R_{stoich}, and the real ratio of their amounts, R_{real}, at an invariant point of the solubility curve, M, on the polarization strength of the cation, P, and its effective polarization strength, P_{ef}, for hydrogen phosphites

Cation	$P \cdot 10^5/pm^{-2}$	$P_{ef} \cdot 10^5/pm^{-2}$	R_{real}	$M = R_{stoich}/R_{real}$
Li^+	16.4	3.55	1.028	0.973
Na^+	10.4	4.92	0.336	2.976
K^+	5.65	5.65	0.303	3.300
Rb^+	4.50	4.50	0.557	1.795
Cs^+	3.67	3.67	0.841	1.189
NH_4^+	4.89	4.56	0.554	1.805
Tl^+	4.50	4.19	0.744	1.344
Mg^{2+}	32.9	4.54	0.456	2.193
Ca^{2+}	17.8	3.07	1.245	0.803
Sr^{2+}	12.4	3.16	1.106	0.904
Ba^{2+}	9.78	3.43	1.066	0.938

ly soluble in water. 3. From the point of view of the polarization strength, the points are distributed nonuniformly, with a large scatter and especially the position of the magnesium cation is exceptional. An approximately linear arrangement of the points is only obtained with the cations that have little effect on water molecules (K^+, Rb^+, Cs^+, NH_4^+, Tl^+). However, with the other cations the selection of the polarization strength is unsuitable and a cation must be selected the size of which corresponds to the concrete situation in saturated aqueous solution. It is obvious from the behaviour of the cations that in selecting the radius of a cation with a strong polarizing effect the cation interaction with water molecules must be considered.

Effect of hydration on the cation polarization strength
and the relationship between the quantities M and P_{ef}

It is generally known that cations are hydrated in aqueous solutions and the mode of hydration variously affects the cation polarization strength, even within a group of cations with similar electron configurations. Hence, for evaluation of the polarizing effect of a cation, its hydration mode must be known. According to the present knowledge, cations are classified from the point of view of hydration into strictors and dilators [23—34]. Strictors strongly affect water molecules in their vicinity and form a hydration sphere. Thus they are often termed positively hydrated cations (Li^+, Na^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). Among dilators are large cations that cannot be accomodated in the cavities of

the water structure and perturb this structure. They exhibit an attraction force toward water molecules, but it is weak in relation to their size and the resultant effect is only a reorientation of water molecules and labilization of the water structure (Rb^+, Cs^+). These cations cannot be considered as having a proper hydration sphere and are termed as negatively hydrated cations. *Samoilov* [23] has demonstrated that strictors maintain water molecules in their neighbourhood in an equilibrium position for a longer time than is the time of their equilibrium position in the structure of water alone; on the other hand, water molecules are maintained for a shorter time in the vicinity of dilators.

It can be seen that the polarization effect of magnesium cation in an aqueous medium is comparable with that of the alkali metal cations, owing to its hydration. The polarizing effect is thus substantially weaker than that of the cation alone. Hence the polarization strength of a cation in an aqueous medium depends on the way of its interaction with water molecules. A hydration sphere is an inseparable part of small cations with two charges, Me^{2+}, and the species $[Me(H_2O)_6]^{2+}$ is formed. This species has been demonstrated in structural studies with many cations, both in aqueous solutions and in a crystalline state [26, 35—41]. The size of such a hydrated cation is virtually the same in solution and in a crystal. With magnesium cation, the size of the species $[Mg(H_2O)_6]^{2+}$ has been given as $r_{ef} = 210$ pm by X-ray structural analysis and its polarization strength, $P = 32.9 \cdot 10^{-5}$ pm^{-2}, decreases to the value of the effective polarization strength, $P_{ef} = 4.54 \cdot 10^{-5}$ pm^{-2}. The other studied strictors do not form such a compact hydration sphere as cation Mg^{2+}, in view of their size and charge, and water molecules in their vicinity are only strongly polarized. This conclusion follows from many properties of aqueous solutions, such as the energy barrier that must be overcome in exchange of water molecules in the hydration sphere [23, 26], the bonding energy of water molecules in the hydration sphere [41], the viscosity coefficient [25, 31, 42—47], and the entropic change of water molecules in the surroundings of cations [48]. The polarization of water molecules with these weaker strictors decreases the favourable effect of the cations on the formation of hydrogen phosphites. In determining the extent of positive hydration of the given cations it is advantageous to relate the polarization strength to that of a cation the effect of which on the neighbouring water molecules is minimal, *i.e.* potassium cation [23, 25, 26, 31, 32, 41, 47] for which it follows from X-ray diffraction [49] that it can replace a water molecule in the structure of an aqueous solution. Hence its effect on water molecules can be neglected and its polarization strength P considered as being equal to effective polarization strength $P_{ef} = 5.65 \cdot 10^{-5}$ pm^{-2}. To assess the changes in the structure of water molecules in the vicinity of the positively hydrated cations Li^+, Na^+, Tl^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}, the change in the entropy of hydration caused by the presence of the cations in the water structure has been selected as

a suitable structural characteristic. The greater this change, the more rigid is the hydration sphere and the weaker is the polarizing influence. On the basis of the values for the change in the entropy of hydration given by *Krestov* [48], the effective polarization strength of these cations, P_{ef}, can be determined from this linear dependence, using the polarization strength of potassium cation as the standard. These polarization strengths are listed in Table 1. The Rb^+ and Cs^+ cations, being dilators, increase the mobility of water molecules in their vicinity and thus their polarizing effect is not influenced by water molecules. This is also confirmed by the change in the entropy of hydration during the formation of their hydration sphere, compared with potassium cation. Their effective polarization strength is only determined by their own size and charge, similar to potassium cation (Table 1). Ammonium cation occupies a special position. In view of its size it should act as a dilator, but the change in the entropy of hydration occurring during its hydration is larger than with potassium cation and its effective polarization strength is somewhat decreased. This decrease can be explained by the formation of a system of hydrogen bonds formed between the ammonium cation and the neighbouring water molecules. The hydration sphere is thus stabilized and the polarizing effect decreased. The set of values obtained for P_{ef} and M is given in Table 1. It was further treated by linear regression from which it follows that the relationship between M and P_{ef} is linear, with a correlation coefficient of $R_k = 0.953$. The linear relationship between effective polarization strength P_{ef} and the composition of saturated aqueous solution at an invariant point on the solubility curve expressed in terms of quantity M, is expressed by the equation

$$M = 1.01(10^5 \cdot P_{ef}/pm^{-2}) - 2.51 \qquad (1)$$

in the studied set of 11 cations.

Discussion

The analysis of the dependence between the polarizing effect of the cations and the composition of saturated solution at invariant points of the solubility curve in ternary systems with phosphite, phosphorous acid, and water indicates that the polarizing effect of the cations favourably influences the formation of hydrogen phosphites and thus also their hydrogen bonding. The effect of the cation positive charge is manifested in a decrease of the electron density at the bond between the phosphorus atom and the oxygen atom in the hydroxyl group and thus its protonation, as the basis for hydrogen bonding between phosphite anions, is facilitated. The stabilization of the hydrogen bond system in hydrogen phosphites thus increases with increasing polarization strength of the cation. Among the cations studied, K^+, Na^+, and Mg^{2+} exhibit the most favourable

effect on the hydrogen bonding and the formation of the hydrogen phosphites. The least favourable effect is exerted by Ca^{2+}, Sr^{2+}, and Ca^{2+} and with them an excess of phosphorous acid over the stoichiometric amount is required for the formation of incongruently soluble hydrogen phosphites. This conclusion on the effect of cations on the formation of hydrogen phosphites from phosphites and phosphorous acid at equilibrium in saturated aqueous solution is in agreement with the results obtained for the changes in the standard Gibbs energy, ΔG° [1, 7]. The largest changes in standard Gibbs energy ΔG° and the most favourable effect on the formation of hydrogen phosphites have been found for K^+, Na^+, and Mg^{2+}, the smallest changes in standard Gibbs energy ΔG° and the least favourable effect on the formation of hydrogen phosphites for Sr^{2+} and Ca^{2+}.

References

1. Lukeš, I. and Ebert, M., *Collect. Czechoslov. Chem. Commun. 45*, 3069 (1980).
2. Lukeš, I., *Thesis.* Charles University, Prague, 1975.
3. Ebert, M. and Škvára, F., *Collect. Czechoslov. Chem. Commun. 29*, 4413 (1964).
4. Ebert, M. and Muck, A., *Collect. Czechoslov. Chem. Commun. 28*, 257 (1963).
5. Ebert, M. and Muck, A., *Chem. Zvesti 18*, 285 (1964).
6. Ebert, M. and Grospietsch, J., *Chem. Zvesti 22*, 578 (1968).
7. Lukeš, I. and Ebert, M., *Collect. Czechoslov. Chem. Commun. 45*, 2283 (1980).
8. Ebert, M. and Grospietsch, J., *Z. Anorg. Allg. Chem. 362*, 225 (1968).
9. Ebert, M., Eysseltová, J., and Rottová, A., *Collect. Czechoslov. Chem. Commun. 35*, 1824 (1970).
10. Ebert, M. and Pelikánová, M., *Collect. Czechoslov. Chem. Commun. 37*, 3672 (1972).
11. Ebert, M. and Kavan, L., *Collect. Czechoslov. Chem. Commun. 41*, 3206 (1976).
12. Ebert, M. and Kavan, L., *Z. Chem. 18*, 36 (1978).
13. Ebert, M. and Eysseltová, J., *Z. Chem. 12*, 189 (1972).
14. Ebert, M. and Kavan, L., *Z. Chem. 18*, 78 (1978).
15. Ebert, M. and Eysseltová, J., *Z. Chem. 8*, 69 (1968).
16. Ebert, M. and Eysseltová, J., *Z. Chem. 7*, 358 (1967).
17. Ebert, M., Vojtíšek, P., and Eysseltová, J., *Z. Chem. 19*, 266 (1979).
18. Ebert, M. and Kavan, L., *Z. Chem. 15*, 493 (1975).
19. Ebert, M. and Kavan, L., *J. Less-Common Metals 81*, 55 (1981).
20. Ebert, M., *DrSc. Thesis.* Charles University, Prague, 1980.
21. Samsonov, G. V., *Fizikokhimicheskie svoistva elementov*, p. 84. Naukova Dumka, Kiev, 1965.
22. Yatsimirskii, K. B., *Thermochemie von Komplexverbindungen*, p. 25. Akademie-Verlag, Berlin, 1956.
23. Samoilov, O. Yu., *Struktura vodnykh rastvorov elektrolitov i gidratatsiya ionov.* Izd. Akad. Nauk SSSR, Moscow, 1957.
24. Robinson, L. A. and Stokes, R. H., *Electrolyte Solutions.* Butterworths Scientific Publications, London, 1959.
25. Gurney, A. W., *Ionic Processes in Solutions.* Dover Publications, New York, 1962.
26. Sinyukov, V. V., *Struktura odnoatomnykh zhidkostei, vody i vodnykh rastvorov elektrolitov.* Nauka, Moscow, 1976.

27. Kavanau, J. L., *Water and Solute—Water Interactions*. Holden-Day, San Francisco, 1964.
28. Izmailov, N. A., *Elektrokhimiya rastvorov*. Izd. Kharkovskogo universiteta, Kharkov, 1959.
29. Shakhporonov, N. I., *Vvedenie v molekulyarnuyu teoriyu rastvorov*. Gos. izd. tekhniko-teoreticheskoi literatury, Moscow, 1956.
30. Conway, B. E., *Ann. Rev. Phys. Chem. 17*, 481 (1965).
31. Conway, B. E. and Barradas, R. G. (Editors), *Chemical Physics of Ionic Solutions*. J. Wiley, New York, 1966.
32. Bockris, J.'O. M. (Conway, B. E., Editor.), *Modern Aspects of Electrochemistry*, Vol. *1*; in Russian translation: *Nekotorye problemy elektrokhimii*. Izd. inostrannoi literatury, Moscow, 1958; Vol. *4*, in Russian translation: *Sovremennye problemy elektrokhimii*. Mir, Moscow, 1971.
33. Mishchenko, K. P. and Poltoratskii, E. M., *Termodinamika i stroenie vodnykh i nevodnykh rastvorov elektrolitov*. Khimiya, Leningrad, 1976.
34. Franks, F. (Editor), *Water*, Vol. *3. Aqueous Solutions of Simple Electrolytes*. Plenum Press, New York, 1973.
35. Wyckoff, W. G., *Crystal Structures*, Vol. *3*. 2nd Edition. Interscience Publishers, New York, 1965.
36. Skryshevskii, A. F., *Rentgenografiya zhidkostei*. Izd. Kievskogo universiteta, Kiev, 1961.
37. Skryshevskii, A. F., *Strukturnyi analiz zhidkostei*. Izd. Vysshaya shkola, Moscow, 1971.
38. Drakin, S. I., Shpakova, S. G., and Pino, X. D., *Fiz. Molekul 2*, 75 (1976).
39. Malenkov, G. G., *Zh. Strukt. Khim. 4*, 102 (1963).
40. Shapovalov, I. M. and Radchenko, I. V., *Zh. Strukt. Khim. 12*, 769 (1971).
41. Yashkichev, V. I., *Zh. Strukt. Khim. 12*, 762 (1971).
42. Kaminsky, M., *Z. Phys. Chem.* (Frankfurt) *5*, 154 (1955).
43. Kaminsky, M., *Z. Phys. Chem.* (Frankfurt) *8*, 173 (1956).
44. Kaminsky, M., *Z. Phys. Chem.* (Frankfurt) *12*, 206 (1957).
45. Kaminsky, M., *Z. Naturforsch. 12a*, 424 (1957).
46. Kaminsky, M., *Discuss. Faraday Soc. 24*, 171 (1957).
47. Kaminsky, M., *Z. Elektrochem. 64*, 867 (1960).
48. Krestov, G. A., *Termodinamika ionnykh protsessov v rastvorakh*, p. 133. Khimiya, Leningrad, 1973.
49. Brady, G. W. and Krause, J. T., *J. Chem. Phys. 27*, 304 (1957).

Translated by M. Štulíková