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Change in the Volume of Orthophosphoric Acid Solutions in the Neutralization with Solutions of Various Bases

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Abstract — Volume changes in the reactions of orthophosphoric acid neutralization with solutions of NaOH, NH_4OH, and tris(hydroxymethyl)methanamine in the mixed solvent H_2O–dimethylformamide were studied by dilatometric titration. Volume effects of the reaction depending on the mixed solvent composition and base strength were discussed.

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Any interparticle interactions (ion–ion, ion–solvent, solvent–solvent) should affect the solution volume characteristics. For reactions in condensed media, it is rather difficult to detect volume effects as they are very small. However, according to Mendeleev [1], "it is possible to judge the chemical nature of dissolution by minute volume changes occurring in solutions." The dilatometric titration is a direct method allowing us to detect minute changes of volumes in any stage of a chemical transformation with a high accuracy [2, 3].

Earlier the dilatometric technique was used in studying volume effects for various reactions: neutralizations of acids with bases [4], protonation of anions [5], complex formation of metal ions with various ligands: Ni(II) with mono-, bi-, and tetradentate ligands [6]; Fe(III) with thiocyanate ions, K^+ with 18-crown, Ni(II) with NH_3 [7]; Ca^{2+}, Li^+, Na^+, and K^+ with ethylenediaminetetraacetic acid (EDTA) [8]; Li^+, Na^+, and K^+ with nitrilotris(methylenephosphonic) acid [9] both in aqueous and in nonaqueous media. The examination of the data obtained allows conclusions on the character of interparticle interactions and on the structure of interacting components of solutions. This method was also applied to heterogeneous systems [10–12]. The evolution of chemical transformations on hydration of cations depending on the concentrations of M^{z+}, ligands, and OH^- on passing from hydrated metal cations in solution to solid-phase oxo–hydroxo compounds was shown.

In this study we examined volume effects in neutralization of weak tribasic orthophosphoric acid in the mixed solvent water–dimethylformamide with the bases NaOH, NH_4OH, and tris(hydroxymethyl)-methanamine (TRIS).

The neutralization of strong protonic acids with alkalis in water (1) is always accompanied by a volume increase ($\Delta V > 0$) [4].

$$H^+ + OH^- \longrightarrow H_2O + \Delta V. \quad (1)$$

The change in volume in this process can be expressed (2) through the corresponding partial molar volumes.

$$\Delta V = \overline{V}_{H_2O} - (\overline{V}_{H^+} + \overline{V}_{OH^-}). \quad (2)$$

As the neutralization of a strong acid with an alkali in water is characterized by $\Delta V > 0$, then $\overline{V}_{H_2O} > (\overline{V}_{H^+} + \overline{V}_{OH^-})$, which is not surprising, as the electrostriction effect makes a significant contribution to the partial molar volumes of ions.

Using available published data on partial molar volumes at infinite dilution [13, 14], we can calculate the corresponding volume change $\Delta V^0 = 18.07 - (-6.4 + 2.4) = 22.07$ cm^3 mol^{-1}, which agrees with the published data [15]. Thus, the calculation also shows that $\Delta V^0 > 0$. The change in the acid strength affects the volume effect of the neutralization reaction. The titration of a weak acid with a strong base in

aqueous solution can be presented by reaction equation (3).

$$HX + OH^- \rightleftarrows H_2O + X^-. \quad (3)$$

This reaction differs from reaction (1) by the fact that it is not accompanied by the variation of the number of ions, as hydroxide anions are replaced by X^- anions [4]. Equation (4) describes the change in volume for this case.

$$\Delta V = (\overline{V}_{H_2O} + \overline{V}_{X^-}) - (\overline{V}_{HX} + \overline{V}_{OH^-}). \quad (4)$$

It follows from Eq. (4) that the value and sign of ΔV will depend on the ratio of the terms $(\overline{V}_{HX} + \overline{V}_{OH^-})$ and $(\overline{V}_{H_2O} + \overline{V}_{X^-})$. We may expect that, the larger the radius of X^-, the weaker the electrostriction effect and the more probable the inequality $\Delta V > 0$. An increase in the anion charge increases the electrostriction effect, which should result in decreasing ΔV.

When polybasic acids are neutralized, the pattern of volume changes becomes more complicated, as the interaction of an acid with an alkali in various neutralization steps is accompanied by volume effects differing in signs and numerical values [16].

The titration of H_3PO_4 with an alkali solution can be presented by Eqs. (5)–(7).

$$H_3PO_4 + OH^- \rightleftarrows H_2O + H_2PO_4^-, \quad (5)$$

$$H_2PO_4^- + OH^- \rightleftarrows H_2O + HPO_4^{2-}, \quad (6)$$

$$HPO_4^{2-} + OH^- \rightleftarrows H_2O + PO_4^{3-}. \quad (7)$$

The results of the dilatometric titration of an aqueous solution of phosphoric acid with sodium hydroxide are shown in Fig. 1, curve *1*. Two sharp bends corresponding to the first two equivalence points are observed in the dilatometric curve. The third step of the H_3PO_4 dissociation is not manifested in the dilatometric curve because of the low value of the dissociation constant (pK_3 12.319 [17]). The neutralization of H_3PO_4 with an alkali in the first two steps is accompanied by an increase in the volume, considerably less pronounced in the second step. Further addition of the base results in a decrease in the volume effect. Thus, we observe a decrease in ΔV with increasing anion charge, as suggested by Eq. (4).

The opposite character of volume changes, as compared to the titration with an alkali solution, is observed when orthophosphoric acid is neutralized with an ammonia solution (Fig. 1, curve *2*). The first step of this reaction can be presented in the ionic form by Eq. (8).

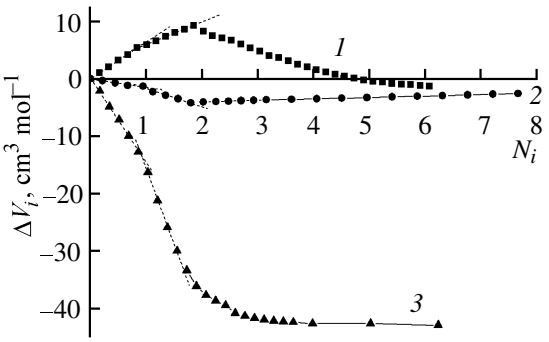

Fig. 1. Curves of dilatometric titration of aqueous H_3PO_4 solution with solutions of (*1*) NaOH, (*2*) NH_4OH, and (*3*) $(HOCH_2)_3CNH_2$.

$$NH_3 + H_3PO_4 \rightleftarrows NH_4^+ + H_2PO_4^-. \quad (8)$$

The negative ΔV indicates that the partial molar volume of the starting components in solution is larger than the partial molar volume of the reaction products $[(\overline{V}_{NH_4^+} + \overline{V}_{H_2PO_4^-}) < (\overline{V}_{NH_3} + \overline{V}_{H_3PO_4})]$ [18]. Unlike reaction (1), in the reaction described by Eq. (8) the reaction products are ionic species, which results in a decrease in the volume ($\Delta V < O$). Two equivalence points corresponding to the dissociation of the acid in two steps were also detected in the titration curve.

The titration of an aqueous solution of H_3PO_4 with a weak base TRIS is also accompanied by a negative volume effect, its value being slightly greater than that in titration with an ammonia solution (Fig. 1, curve *3*). The shape of the plot $\Delta V = f(N)$ suggests that the dissociation of the acid also passes in two steps, although the dilatometric curve demonstrates a smooth volume change rather than a well-defined sharp bend corresponding to the second step of the neutralization. In this connection, we have carried out the potentiometric titration of H_3PO_4 with a TRIS solution (Fig. 2). Figrue 2 shows that only one equivalence point is observed in the potentiometric curve, which corresponds to the first step of the acid dissociation.

The considerable negative effect can be caused by the strong intermolecular interactions resulting in the formation of either a hydrogen-bonded complex of phosphoric acid with TRIS ($RNH_2 \cdots H_3PO_4$) or an ion pair ($RNH_3^+H_2PO_4^-$).

The titration of H_3PO_4 with sodium hydroxide in the mixed solvent water–dimethylformamide was accompanied by precipitate formation. As the content of dimethylformamide in the mixture increased, the

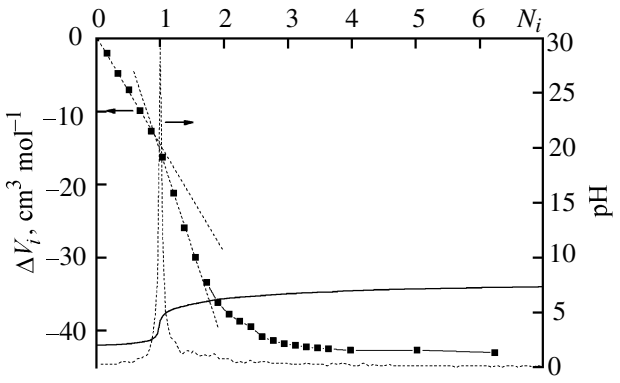

Fig. 2. Dilatometric and potentiometric titration curves of aqueous phosphoric acid solution with TRIS. The dotted line is the differential potentiometric curve.

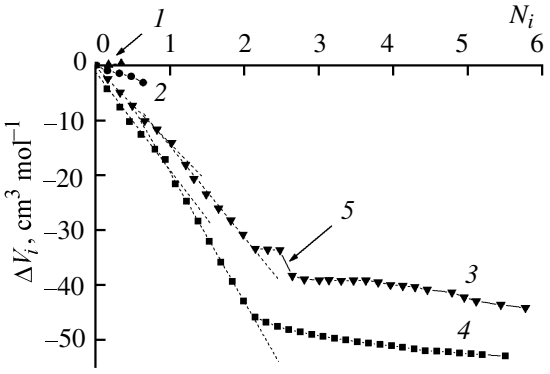

Fig. 3. Changes in volume of solutions in the course of H_3PO_4 titration with sodium hydroxide in H_2O–DMF solvent. DMF mole fraction: (*1*) 0.5, (*2*) 0.3, (*3*) 0.2, and (*4*) 0.05; (*5*) precipitation.

precipitation occurred at smaller amounts of the titrant added. At a DMF mole fraction in solution of 0.5, the precipitate was formed even at the very beginning of the titration. Probably, sodium dihydrogen phosphate is precipitated, as its solubility even in pure water is limited (85.2 g per 100 g of water at 20°C [19]).

The curves of the titration up to the onset of precipitation (except for the solution with the dimethylformamide mole fraction of 0.2) are shown in Fig. 3.

It is known that salts of alkali metals readily dissociate in dimethylformamide [20, 21]; therefore, we assumed that NaOH used in the titration in the H_2O–DMF mixture is also a strong electrolyte. In this connection, the process of titration in the mixed solvent is described by Eqs. (5)–(7).

Figure 3 also shows that the addition of DMF to water changes the sign of the reaction volume effect for the opposite in comparison with the reaction in aqueous solution. This fact may be due to heteroselective solvation in the mixed solvent: The acid is preferentially solvated with *N,N*-dimethylformamide molecules having stronger basic properties (proton affinity *PA* 887.5 kJ mol^{-1} [22]) as compared to water (*PA* 691 kJ mol^{-1} [22]), whereas anions are solvated with water molecules. Then Eq. (5) transforms to expression (9).

$$(H_3PO_4)_{Sol} + OH^-_{aq} \longrightarrow H_2O + (H_2PO^-_4)_{aq} + Sol - \Delta V. \quad (9)$$

In this process we observe resolvation: Acid molecules were solvated with dimethylformamide molecules, and the acid anion, with water. Furthermore, the partial molar volume of water in the H_2O-DMF mixture is smaller than that in pure water [23], which can also result in decreasing ΔV.

As the DMF content increases, the volume effect decreases (Fig. 3). This is attributable to a change in the dependence of the partial molar volumes of reaction (9) components on the composition of the mixed solvent. The partial molar volumes of DMF and H_2O strongly change over the range of compositions under study (Fig. 4), which can determine the position of titration curves with increasing DMF content in the mixture.

It is also seen from Fig. 3 that the phosphoric acid dissociation in the mixtures under study occurs in two steps. At a DMF mole fraction in the solution of 0.2, the volume effect sharply increases after the second equivalence point, which is due to the precipitation of sodium dihydrogen phosphate. On further adding the titrant, the precipitate dissolved, which was caused by the conversion of sodium dihydrogen phosphate to disodium hydrogen phosphate, which is much more soluble in water.

It is rather difficult to select a soluble base for the titration of acids in anhydrous DMF. In titration of H_3PO_4 both with tris(hydroxymethyl)methanamine soluble in DMF and with an alkali in a mixed solvent, a precipitate was formed, which hampered the analysis of the dilatometric curve. At the same time, it should be noted that the process was accompanied by a considerable decrease in volume.

Thus, our study shows that the neutralization of acids is accompanied by a change in volume. Its value and sign are determined by both the properties of the solvent and the strength of the acid and base involved in the reaction.

EXPERIMENTAL

We prepared 100% orthophosphoric acid from the chemically pure grade 85% acid and chemically pure grade phosphorus pentoxide (P_2O_5) by concentrating.

The acid concentration was monitored by the potentiometric titration with a NaOH solution and by density [24].

Chemically pure grade dimethylformamide was subjected to double vacuum distillation (P 133 Pa) at 310 K, and the middle fraction was collected. The distilled solvent was dehydrated over 4 Å molecular sieves for 72 h and distilled again, with collection of the middle fraction (60% of the total amount). The water content of dimethylformamide, according to amperometric Fischer titration, did not exceed 0.03 wt%. Solutions were prepared by weight.

The dilatometric titration was carried out at 298 ± 0.01 K on a dilatometer-titrator. Its scheme and operating principle have been described previously [2]. The volume changes in reactions were detected by a shift of the meniscus in a capillary with a diameter of 0.4 mm. The experimental data are presented in the form of the plot of volume changes ΔV_i vs. molar ratios $N = c_{base}/c_{acid}$. The values of ΔV_i and N for each point of the titration were calculated by relationships (10) and (11).

$$\Delta V_i = \frac{\Delta S_i V_{1cm} \times 10^{-3}}{V_0 c_{acid}}, \text{ cm}^3 \text{ mol}^{-1}, \quad (10)$$

$$N_i = \frac{U_i V_{1rev} c_{base}}{V_0 c_{acid}}, \text{ equiv mol}^{-1}. \quad (11)$$

Here $\Delta S_i = S_i - S_0$ is the meniscus shift, cm; V_{1cm}, volume of 1 cm of the capillary (for the capillary in use it was 1.261×10^{-3} cm^3); V_0, initial volume of the bottom chamber, 41.76 cm^3; c_{acid}, acid concentration, M; U_i, number of revolutions of the dilatometer rod; V_{1rev}, volume of liquid corresponding to one revolution of the rod; and c_{base}, concentration of the titrating base, M.

For the titration of phosphoric acid in water we used NaOH, NH_4OH, and TRIS solutions as titrants; for the titration in the H_2O–DMF mixture, a NaOH solution; and for the titration in an anhydrous DMF solution, a TRIS solution.

In most cases the experimental dilatometric curves can be presented by rectilinear segments with bend points corresponding to integer numbers of the base equivalents added per mole of the acid.

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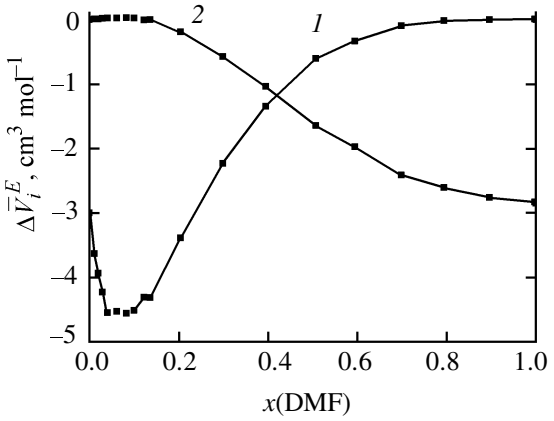

Fig. 4. Excess partial molar volumes of H_2O and DMF in H_2O–DMF mixture at 298.15 K [23]. (*1*) DMF and (*2*) H_2O.

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