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Raman Studies on Species in Single and Mixed Solutions of Molybdate and Vanadate

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Raman spectroscopy was applied to investigate the speciation in both single and mixed solutions of molybdate and vanadate at pH values from 10.0 to 1.0. Evidence was obtained for the difference of existing forms between these two elements. Vanadium mainly exists as $(VO_3)_n{}^{n-}$ while Mo is $MoO_4{}^{2-}$ in the pH range of 9.0−7.5. This difference is the theoretical basis for many available separation process. The species in the binary system was identified by comparing the Raman spectra with that in the single systems. Molybvanadates are formed below pH=6.5, which may partly be ascribed to the replacement of V atoms by Mo atoms in some V-O-V groups. Vanadium mainly exists as the decavanadate species in the pH range of 6.0−2.0. The predominant species of Mo are heteropolyanions having structural features of heptamolybdate rather than $Mo_8O_{26}{}^{4-}$ and $Mo_{36}O_{112}{}^{8-}$ which are the predominant Mo species in single solution at pH=2.0−1.0.

Key words: Raman spectroscopy, Molybvanadates, Molybdenum, Vanadium, Existing form

I. INTRODUCTION

Presently, kinds of untraditional resources such as Ni−Mo ores, spent hydrodesulphurisation catalysts and alloy scrap, have to be utilized with the continuous consumption of high-grade molybdenum and vanadium ores [1, 2]. Frequently, these resources contain both molybdenum and vanadium. As a result, separation of Mo and V has been increasingly important.

Any technique used for the separation of similar elements must take advantage of the small differences between them [3]. In fact, there have been differences in the existing forms between Mo and V in aqueous solution at a certain pH. Based on this, considerable research efforts have been devoted to separating Mo and V from mixed solution by precipitation, solvent extraction, ion exchange, and adsorption. However, due to the limited research for the Mo-V-H_2O system, such approaches were always inspired and explained by the knowledge of the single Mo-H_2O and V-H_2O systems. But the real mixed solution system is not the simple superposition of single systems, because the formation of molybvanadate ions occurs in the acid condition [4, 5]. As a result, the existing forms of Mo and V in the binary system are greatly different from that in the single system.

Zhang *et al.* have investigated the species distribution at different pH in the Mo-V-H_2O system according to thermodynamic calculation [6]. The real situation will be further clarified if some verification experiments are conducted.

Raman spectroscopy, as a modern analytical technique, has been widely used to study the speciation of predominant species formed in aqueous solution. The single molybdate [7, 8] and vanadate [9] solutions have been investigated by Raman spectroscopy with a view to establish the species variation with the pH change of the solution. However, they have not agreed on the dominant species in the whole acidification process. So far, the Raman analysis for the mixed solutions have not been reported.

In this work, the species at different pH were characterized in both single and mixed solutions of molybdate and vanadate by Raman spectroscopy. The species in the binary system, especially the molybvanadate ions was identified by comparing the Raman spectra with that of the single systems. Particularly, we have clarified the difference in existing forms between these two elements, and it could provide theoretical basis for the Mo-V separation process.

II. METHODS

The test solutions were prepared by diluting 1 mol/L of stock solutions of Mo and V. Stock solution of Mo was obtained by dissolving the exact quantities of $Na_2MoO_4{\cdot}2H_2O$(Sinopharm Chemical Reagent Co. Ltd., China), while vanadate solution was obtained

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by dissolving V_2O_5 (Tianjin Fuchen Chemical Reagent Factory, China) with NaOH solution. The concentrations of Mo and V in the single and mixed solutions were both maintained at 0.35 mol/L, although at low pH, precipitation of solid materials made it difficult to maintain a known concentration accurately. Before diluting, the pH of each test solution was adjusted to the required value. Measurements of pH were made using pH meter (Shanghai Leici Instrument Plant, China) over pH range of 10.0−1.0.

Raman spectra were recorded for the test solutions kept in sealed quartz capillary with a Raman spectrometer (LabRAM HR Evolution, HORIBA, France). Raman spectra were excited by a 532 nm diode pumped solid state laser at a resolution of 0.65 cm^{-1} in the range of 400−1100 cm^{-1}. Hydrochloric acid was used to control the pH since it has no appreciable Raman spectrum of its own [10].

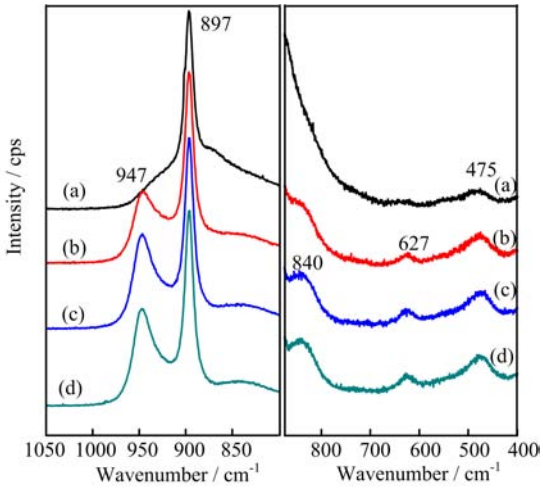

FIG. 1 Raman spectra of the mixed solutions at alkaline pH range ([Mo]=0.35 mol/L, [V]=0.35 mol/L). (a) pH=10.0, (b) pH=9.0, (c) pH=8.0, (d) pH=7.5.

III. RESULTS AND DISCUSSION

A. Raman spectra of the mixed solutions of molybdate and vanadate at alkaline pH

As it is well known, molybvanadate ions are formed in the acid condition, so the species of Mo or V are almost the same in the single and mixed solutions at alkaline pH. Figure 1 shows the Raman spectra for the mixed solutions of Mo and V at pH values of 10.0−7.5. It must be noted that the intensity of Raman peaks at 900−1050 cm^{-1} is much higher than that at 400−800 cm^{-1}, the whole spectrum was placed into two coordinate systems with different ranges of vertical axis, in order to observe every Raman line clearly (the same below). At pH=10.0, only one evident peak at 897 cm^{-1} was observed, which is assigned to mononuclear molybdate ion $MoO_4{}^{2-}$ [11]. Additionally, this peak essentially unchanged when pH decreased to 7.5, indicating that the existing form of Mo is only $MoO_4{}^{2-}$ at pH=10.0−7.5. Four new Raman peaks existed at pH=9.0. One was stronger at 947 cm^{-1} and an increase in intensity was observed from pH=9.0−8.0, the others were weak at 840, 627, and 475 cm^{-1}. These four peaks are all assigned to the $(VO_3)_n{}^{n-}$ [12]. It indicates that V mainly exists as the polymeric ion $(VO_3)_n{}^{n-}$ in the pH range of 9.0−7.5.

Therefore, we can conclude that V has higher polymerization tendency than Mo. Compared with the monomeric $MoO_4{}^{2-}$ ions, the polymeric $(VO_3)_n{}^{n-}$ has a higher electrovalence, so they are expected to be preferentially separated from molybdate solution by using suitable separation reagents. Interestingly, many available methods like solvent extraction [13, 14] and ion exchange [15, 16] are based on this principle, and the optimum pH values for these methods are just in the range of 9.0−7.5.

B. Raman spectra of the single solutions of molybdate and vanadate (pH=7.0−1.0)

In the acid pH range, Raman analysis was first carried out for the single Mo and V solutions, then we can find out the difference of existing forms in the single and binary systems by comparing Raman spectra. Figure 2 shows the Raman spectra of the molybdate solutions in the pH range of 7.0−1.0. As pH=7.0, only a Raman peak was observed at 897 cm^{-1} assigned to $MoO_4{}^{2-}$. A new Raman peak appeared at 940 cm^{-1} with a decrease in the intensity of the 896 cm^{-1} peak. The peak at 940 cm^{-1} is assigned to $Mo_7O_{24}{}^{6-}$ [17], indicating the polymerization of $MoO_4{}^{2-}$ occurs below pH=7.0 when the concentration of Mo is 0.35 mol/L. As pH=4.0, the peak at 896 cm^{-1} almost disappeared while the peak at 940 cm^{-1} was shifted to the wavenumber at 948 cm^{-1}. This change may well be due to the protonated species $HMo_7O_{24}{}^{5-}$ and $H_2Mo_7O_{24}{}^{4-}$. As pH was lowered to 2.0, there appeared three new peaks. By comparing with the Raman spectra of solid samples in Ref.[18], the peak at 957 cm^{-1} is assigned to α-$Mo_8O_{26}{}^{4-}$ and the peaks at 970 and 908 cm^{-1} are assigned to β-$Mo_8O_{26}{}^{4-}$, respectively. As pH was lowered further, the intensity of the peak at 957 cm^{-1} increased, and simultaneously there appeared two evident peaks at 902 and 983 cm^{-1}. These three Raman peaks are all ascribed to $Mo_{36}O_{112}{}^{8-}$, as also found by Tytko *et al.* [19]. Additionally, a weak Raman peak was observed at 851 cm^{-1} which may be assigned to $MoO_2{}^{2+}$ [20]. On this basis, the dominant species is $Mo_{36}O_{112}{}^{8-}$ rather than $MoO_2{}^{2+}$ in the 0.35 mol/L molybdate solution at pH=1.0.

The distribution of Mo species as a function of pH was calculated and shown in Fig.3. The relevant equilibrium constants were given in Ref.[21] and the detailed calculation method can be re-

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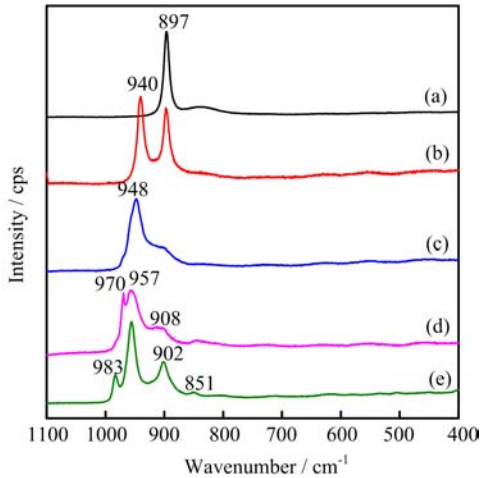

FIG. 2 Raman spectra of the molybdate solutions as a function of pH ([Mo]=0.35 mol/L). (a) pH=7.0, (b) pH=6.0, (c) pH=4.0, (d) pH=2.0, (e) pH=1.0.

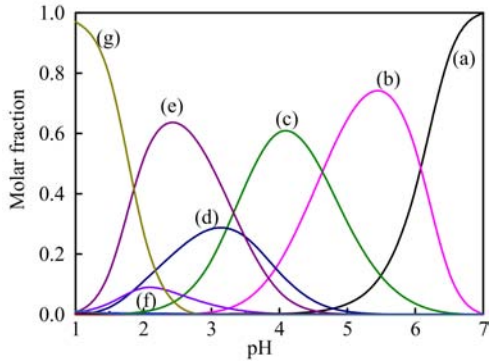

FIG. 3 Molar fraction of Mo in main ions as a function of pH in solutions of 0.35 mol/L Na_2MoO_4 (25 °C). Calculations are based on Ref.[21]. (a) MoO_4^{2-}, (b) $Mo_7O_{24}^{6-}$, (c) $HMo_7O_{24}^{5-}$, (d) $H_2Mo_7O_{24}^{4-}$, (e) $Mo_8O_{26}^{4-}$, (f) $H_3Mo_7O_{24}^{3-}$, and (g) $Mo_{36}O_{112}^{8-}$.

ferred to Ref.[6]. From the calculation result, the species existing as the predominant species in the 0.35 mol/L molybdate solution can be concluded as follows: MoO_4^{2-}(pH>6.1)→$Mo_7O_{24}^{6-}$(6.1>pH>4.7)→$HMo_7O_{24}^{5-}$(4.7>pH>3.3)→$Mo_8O_{26}^{4-}$(3.3>pH>1.8)→$Mo_{36}O_{112}^{8-}$(1.8>pH>1.0). Interestingly, this result is in good agreement with the result of Raman analysis.

The Raman spectra of the vanadate solutions in the pH range of 7.0−1.0 are shown in Fig.4. As pH=7.0, the strongest Raman peak at 947 cm^{-1} was due to $(VO_3)_n^{n-}$, while the weaker peaks at 840, 627, 475 cm^{-1} (Fig.1), ascribed as $(VO_3)_m^{n-}$, were replaced by the peaks at 830, 592, 464 cm^{-1}. Among them, the peaks at 830 and 464 cm^{-1} are assigned to asymmetric and symmetric stretches of V-O-V group [18, 22]. These new peaks, together with the peak at 988 cm^{-1} (V=O group), are ascribed to $V_{10}O_{28}^{6-}$ [23]. As pH dropped to 6.0, the Raman peaks essentially unchanged. While

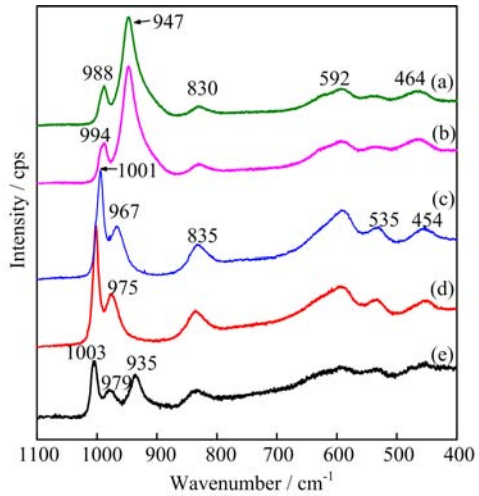

FIG. 4 Raman spectra of the vanadate solutions as a function of pH ([V]=0.35 mol/L). (a) pH=7.0, (b) pH=6.0, (c) pH=4.0, (d) pH=2.0, (e) pH=1.0.

as pH lowered further, the peaks of $(VO_3)_m^{n-}$ disappeared and two new peaks at 535 and 967 cm^{-1} were observed. Additionally, the peaks at 988, 830, 464 cm^{-1} were shifted to 994, 835, 454 cm^{-1}. The said effect may well be due to the present of protonated species $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ [9]. As pH lowered further, the wavenumbers of 994 and 967 cm^{-1} peaks continued to increase due to the protonation effect. It must be noted that the precipitation of V_2O_5 occurred in the 0.35 mol/L vanadate solution at pH=1.0, so the quality of the spectrum was not as high as that of the others. However, a new Raman peak was observed at 935 cm^{-1} which may be tentatively ascribed to the formation of VO_2^+ [24].

The distribution of V species in the pH range of 10.0−2.0 was calculated and shown in Fig.5. According to the calculation result, the transformation course approximately coincides with the Raman results, except that the predominant species is $(VO_3)_m^{n-}$ rather than decavanadate ions at pH=6.0.

C. Raman spectra of the mixed solutions of molybdate and vanadate (pH=7.0−1.0)

The Raman spectra of mixed solutions of molybdate and vanadate at different pH values from 7.0 to 5.5 are shown in Fig.6. The spectrum at pH=7.0 changed little compared with that at pH=7.5 (Fig.1). As pH lowered to 6.5, the Raman peak at 897 cm^{-1} decreased in intensity due to the polymerization of MoO_4^{2-}. Simultaneously, a new Raman peak appeared at 988 cm^{-1} and other three peaks shifted to 470, 590, 834 cm^{-1}, ascribed to the formation of $V_{10}O_{28}^{6-}$. Such behaviors of existing forms are almost consistent with that in the single molybdate and vanadate solutions, indicating the mutual effect of Mo and V is weak above

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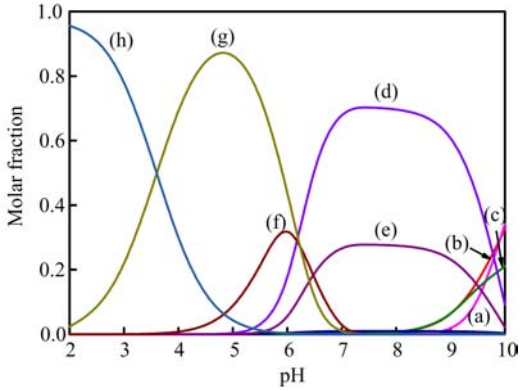

FIG. 5 Molar fraction of V in main ions as a function of pH in solutions of 0.35 mol/L Na_3VO_4 (25 °C). Calculations are based on Ref.[25]. (a) $V_2O_7^{4-}$, (b) HVO_4^{2-}, (c) $HV_2O_7^{3-}$, (d) $V_4O_{12}^{4-}$, (e) $V_5O_{10}^{5-}$, (f) $V_{10}O_{28}^{6-}$, (g) $HV_{10}O_{28}^{5-}$, (h) $H_2V_{10}O_{28}^{4-}$.

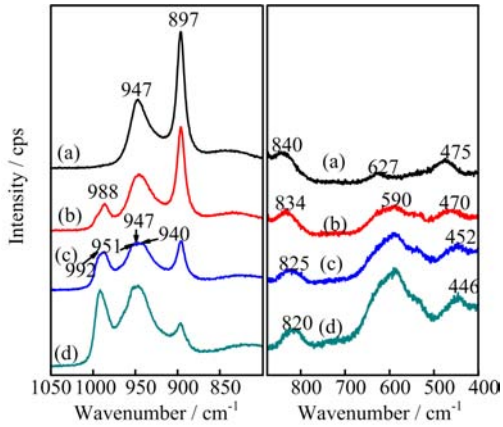

FIG. 6 Raman spectra of the mixed solutions at pH range from 7.0 to 5.5 ([Mo]=0.35 mol/L, [V]=0.35 mol/L). (a) pH=7.0, (b) pH=6.5, (c) pH=6.0, (d) pH=5.5.

pH=6.5. As pH continued to decrease, the Raman peak of MoO_4^{2-} tends to diminish, but the peak at 940 cm^{-1} due to heptamolybdate merged into the peak at 947 cm^{-1}. With the polymerization of MoO_4^{2-}, the merged peak was broaden gradually, and could be separated into three peaks at 940, 947, 951 cm^{-1} at pH=5.0. Additionally, the peak of V=O group shifted from 988 cm^{-1} to 992 cm^{-1} and the peak at 590 cm^{-1} essentially unchanged, as it occurred in the single vanadate solution. However, the peaks assigned to asymmetric and symmetric stretches of V−O−V group shifted from 470, 834 cm^{-1} to 446, 820 cm^{-1}, respectively. It may indicate that Mo atoms replace V atoms in some V−O−V groups, and as a consequence, molybvanadates are formed at pH=6.5−5.5. Apparently, Mo and V cannot be efficiently separated in this pH range by the traditional separation process.

Figure 7 shows the Raman spectra of the mixed solutions of molybdate and vanadate at pH=5.0−1.0. The

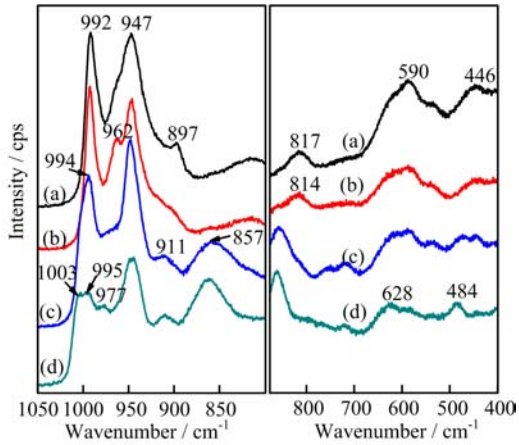

FIG. 7 Raman spectra of the mixed solutions at pH range from 5.0 to 1.0 ([Mo]=0.35 mol/L, [V]=0.35 mol/L). (a) pH=5.0, (b) pH=4.0, (c) pH=2.0, (d) pH=1.0.

Raman peak at 947 cm^{-1} diminished gradually, but it still existed even at pH=1.0. As it shows in the Raman spectra of single molybdate and vanadate solution, there is no Raman peak around 947 cm^{-1} below pH=2.0. Thus, we may tentatively consider that Mo mainly exists as heteropolyanions, having structural features of heptamolybdate, rather than $Mo_8O_{26}^{4-}$ and $Mo_{36}O_{112}^{8-}$ which are the predominant Mo species in molybdate solution at pH=2.0−1.0. The Raman peaks assigned to V=O group in decavanadate shifted from 962, 992 cm^{-1} to 977, 1003 cm^{-1} due to the protonation effect. However, the intensity of these peaks, together with other peaks (446, 590 cm^{-1}) due to decavanadate decreased with lowering of pH. This is partly ascribed to the precipitation of V_2O_5 and also due to the formation of VO_2^+ which can be verified by the Raman peak at 917 cm^{-1}. Simultaneously, there also appeared several new peaks at 857, 628, and 484 cm^{-1} in the strong acid solution. The first one is associated with the presence of MoO_2^{2+}, but no evidences have been found to identify the last two peaks.

IV. CONCLUSION

The species at different pH were characterized in both single and mixed solutions of molybdate and vanadate by Raman spectroscopy. The predominant species in the 0.35 mol/L molybdate solution at different pH is MoO_4^{2-} (pH>6.1), $Mo_7O_{24}^{6-}$ (pH=6.1−4.7), $HMo_7O_{24}^{5-}$ (pH=4.7−3.3), $Mo_8O_{26}^{4-}$ (pH=3.3−1.8), $Mo_{36}O_{112}^{8-}$ (1.8−1.0), while in the single vanadate solution with the same concentration, the species order is $(VO_3)_m^{n-}$, $V_{10}O_{28}^{6-}$, protonated decavanadate as pH from 9.5 to 2.0. Evidence was obtained for the result that vanadium has higher polymerization tendency than molybdenum. Based on this difference, molybdenum and vanadium are expected to be separated in

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the pH range of 9.0−7.5. In the mixed solution below pH=6.5, the replacement of V atoms by Mo atoms in some V−O−V groups leads to the shift of corresponding Raman peaks, indicating the formation of molybvanadates. Molybdenum mainly exists as heteropolyanions having structural features of heptamolybdate while vanadium exists as the decavanadate species in the pH range of 6.0−2.0.

V. ACKNOWLEDGMENTS

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