

## DIFFUSION COEFFICIENTS OF POTASSIUM CHROMATE AND DICHROMATE IN WATER AT 25°C

Václav VACEK<sup>a</sup> and Vladimír ROD<sup>b</sup>

<sup>a</sup> *Department of Chemical Engineering,*

*Prague Institute of Chemical Technology, 166 28 Prague 6 and*

<sup>b</sup> *Institute of Chemical Process Fundamentals,*

*Czechoslovak Academy of Sciences, 165 02 Prague 6*

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The concentration dependences of diffusion coefficients of potassium chromate and dichromate in water at 25°C were measured by using the Taylor technique of the concentration pulse dispersion in laminar flow of liquid. The results were compared with hitherto published mutually inconsistent data for potassium and sodium chromates and dichromates.

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Merely two independent sets of diffusion coefficients in water have been published up to now for potassium chromate and dichromate which, however, significantly differ: The older Ohlm data<sup>1,2</sup> presented as well in standard monographs<sup>3-5</sup> are as much as several times higher for potassium dichromate than the data measured independently by Mansour and coworkers<sup>6</sup>. The diffusion coefficients of sodium chromate and dichromate exhibit similar character: The data due to Ohlm<sup>1-2</sup> (see also refs<sup>3-5</sup>) are 20–30% higher than those published later by Ball and Oldham<sup>7</sup>. It is interesting as well that the conclusions in both the latter papers<sup>6,7</sup>, whose authors were not aware of the existence of the works of their predecessor<sup>1-2</sup>, may be incorrect owing to the used logic of their deduction. Ball and Oldham<sup>7</sup> assume tacitly that the diffusivity of dichromates is considerably lower than that of chromates as a consequence of geometric size of anion, thus not allowing for hydration effects which apparently manifest themselves significantly<sup>3</sup>. From an overall decrease of diffusivity of sodium chromate in alkaline medium which does not occur in acidic media, Ball and Oldham<sup>7</sup> draw the conclusion that the chromate ion dimerization does not manifest itself significantly in solutions of chromates. The detailed analysis of equilibrium of the dimerization reaction on the basis of spectrophotometric investigation of light absorption in solutions of chromates<sup>8</sup> remained also unnoticed by those authors<sup>7</sup>.

The lower values of diffusion coefficients of potassium dichromate in comparison with chromate as measured by Mansour and coworkers<sup>6</sup> do not agree with the Ohlm data<sup>1,2</sup> when, for both the pairs of chromates and dichromates (for sodium and potassium salts), slightly higher diffusivities of dichromates were found than for

chromates<sup>1-5</sup>, especially in more concentrated solutions. Moreover, the unusual form of concentration dependence of diffusion coefficients found by Mansour and coworkers<sup>6</sup> is by itself a sufficient reason for reinvestigation. Mansour and coworkers<sup>6</sup> claim that a similar shape of the dependence was found for a number of further electrolytes, however, this claim was not proved by the literature search carried out in the framework of this work. For instance, in the data collections<sup>5,9,10</sup> there is not a single similar case.

## EXPERIMENTAL

The experiments were carried out and evaluated by the same method<sup>11</sup> and by using the same apparatus<sup>12</sup> as in measuring the diffusion coefficient of potassium chlorate published in our foregoing paper<sup>11</sup>.

Doubly recrystallized salts, originally of *p.a.* grade (Lachema, Brno, Czechoslovakia), were dried over P<sub>2</sub>O<sub>5</sub> in a desiccator. For the purification by recrystallization, water redistilled in a quartz apparatus was used. The prepared aqueous solutions of chosen concentrations were employed as a carrier electrolyte stream.

The samples for the injection were prepared by diluting the carrier solutions. The concentration difference between the carrier solutions and the injected solutions were 0.05–0.09 mass%. With regard to these small concentration differences, the measurements are performed at practically constant concentration, the secondary effects due to the heat of solution or volume changes may be neglected, and the measured value of diffusion coefficient corresponds to the differential diffusion coefficient as defined by Fick's law.

For each concentration level, the number of the experiments was chosen (always four times) in accordance with preliminary experiments in which the difference between the highest and lowest found values was 2–3%. The arithmetic averages of the four measurements are given as the results below. In one case when the difference of the lowest and highest value was 10.2%, all the series of four measurements was cancelled and repeated so that in all the cases presented, the variation of the lowest and highest values was lower than 3%. This range corresponds to the expected uncertainty which follows from the detailed analysis of possible errors of individual steps of the used measuring method given in works by Baldauf and Knapp<sup>13</sup> and Alizadeh and coworkers<sup>14</sup>.

The values of diffusion coefficients taken from the literature for 20°C were converted to the values for 25°C by using the temperature dependence given in monograph<sup>4</sup>. To express the concentrations of solutions, the published values of molarity (*c*) were converted to molality (*m*) by means of the concentration dependence of density of the potassium dichromate solutions given also in monograph<sup>4</sup>.

## RESULTS AND DISCUSSION

The measured values of differential diffusion coefficients for potassium chromate in water are illustrated in Fig. 1 and for potassium dichromate in Fig. 2. In both the cases, the measured data agree practically completely with the course of concentration dependence of diffusion coefficients of the Ohlm data<sup>1,2</sup> (cited according to works<sup>3-5</sup>). So, the original finding<sup>1,2</sup> of higher diffusivities of dichromates in

comparison with chromates is directly proved. This was found by Oholm<sup>1,2</sup> also for the sodium salt as illustrated in Fig. 3. The explanation due to Jander and Spandau<sup>3</sup> lies in considering hydration: The dichromate anion is substantially less hydrated in comparison with the chromate anion so that its effective size which manifest itself in diffusion phenomena may be smaller than that for the hydrated chromate ion. This idea is independently proved, *e.g.*, when analyzing the concentra-

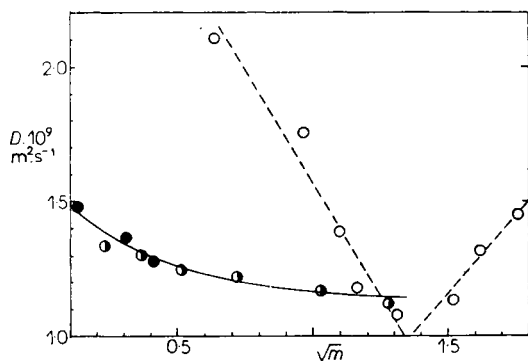


FIG. 1

Concentration dependence of diffusion coefficient of potassium chromate in water at 25°C; ● this work, ◐ Oholm<sup>1,2</sup>, ○ Mansour and coworkers<sup>6</sup>

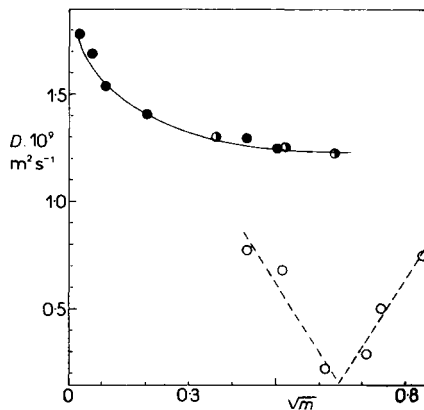


FIG. 2

Concentration dependence of diffusion coefficient of potassium dichromate in water at 25°C; ● this work, ◐ Oholm<sup>1,2</sup>, ○ Mansour and coworkers<sup>6</sup>

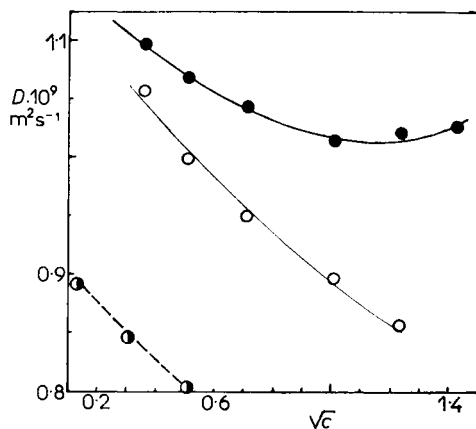


FIG. 3

Concentration dependence of diffusion coefficient of sodium chromate and dichromate in water at 25°C; ● Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Oholm<sup>1,2</sup>, ○ Na<sub>2</sub>CrO<sub>4</sub> Oholm<sup>1,2</sup>, ◐ Na<sub>2</sub>CrO<sub>4</sub> Ball and Oldham<sup>7</sup>

tion dependences of heats of solution of potassium chromate and dichromate<sup>15</sup>. A conspicuous difference is evident between the strongly endothermic dissolution of salts with a doubled anion ( $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{S}_2\text{O}_8^{2-}$ ) and the weakly endothermic dissolution of corresponding single anions ( $\text{CrO}_4^{2-}$  and  $\text{SO}_4^{2-}$ ). It demonstrates a weaker exothermic hydration of doubled anions compared to the corresponding single anions. This effect can be expected considering the analogy to the dependence of degree of cation hydration (of the same charge) on their size<sup>3,9</sup>.

Considering the mutual consistency of the measured diffusion coefficients with the data of Ohlm for both the salts investigated (Figs 1 and 2) as well as the consistency with his data<sup>1-5</sup> for sodium salts (Fig. 3), it is possible to regard the data due to Mansour and coworkers<sup>6</sup> as unreliable and the data by Ball and Oldham<sup>7</sup> as inaccurate.

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