THE TRANSFERENCE NUMBERS OF KBr AND KI IN AQUEOUS SOLUTION

AT 15, 25 AND 40°C UP TO 1,500kg/cm²

By Jiro Osugi*, Masaru Nakahara*, Yasuhiko Matsubara*
and Kiyoshi Shimizu**

The moving boundary method devised by Wall and Gill[1] has been employed to measure the cation transference numbers of KBr and KI in 0.01 N solution at high pressures up to 1,500 kg/cm² (1 kg/cm² =0.9678 × 10⁵ Pa).

At each temperature, the cation transference number of KBr decreases gradually with increasing pressure like the 1-1 electrolytes studied until now, such as KCl, NaCl and NH₄Cl. It does not level off in the pressure range of 500 to 1,000 kg/cm², in contrast to the result by Wall and Berkowitz[2]. The cation transference number of KI, on the other hand, increases with the rise in pressure up to 1,500 kg/cm² at all the temperatures studied. apparently like HCl.

The temperature and pressure coefficients of the cation transference number are the same in sign for KBr as found in the case of KCl by Kay et al.[4], but opposite for KI.

Introduction

The transference numbers are required to be known at high pressures so that the conductivity method can be sufficiently powerful for the studies of ionic solutions under high pressures. In 1955 Wall and Gill[1] first succeeded in the modification of the conventional moving boundary method so as to measure the transference numbers under high pressures. They found the cation transference numbers of 0.1N solutions of KCl and NaCl decreased and that of HCl increased at 25°C, as pressure increased up to 1,000 bar. In 1958 Wall and Berkowitz[2] reported the cation transference numbers of KCl. NaCl. NH₄Cl and KBr in aqueous solutions about fivefold more dilute than the first, and found that the dependence of transference number on pressure was relatively independent of the concentration. In 1965 Hills. Ovenden and Whitehouse[3] successfully adapted the electromotive force method to high pressure, and measured the transference number of HCl in water at infinite dilution at 25 and 45°C up to 2,000 atm. In 1970 Kay, Pribadi and Watson[4] utilized Wall and Gill's method to give more reliable values of the transference number of KCl in water at 25°C up to 2,000 bar, which were

1) F.T. Wall and S.J. Gill, J. Phys. Chem., 59, 278 (1955)
2) F.T. Wall and J. Berkowitz, ibid., 62, 87 (1958)
3) G.J. Hills, P.J. Ovenden and D.R. Whitehouse, Discuss. Faraday Soc., 39, 207 (1965)
4) R.L. Kay, K.S. Pribadi and B. Watson, J. Phys. Chem., 74, 2724 (1970)

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cited by Hamann[5] to calculate the limiting equivalent conductivities of K^+ and Cl^- ions at high pressures. In 1972 Pribadi[6] designed a new type of moving boundary detector with probe electrodes on the outside of a moving boundary tube. which was declared to allow the transference number to be measured with an extremely high precision up to 3,000 bar. In 1973 Matsubara, Shimizu and Osugi[7] made use of the Wall and Gill method to measure the transference number of KCl in water at high pressures and at various temperatures, found that the degree of the decrease in the cation transference number of KCl with increasing pressure was much reduced by the increase in temperature from 15 to 40°C.

In the present communication, we report the temperature influence on the pressure dependence of the transference numbers of KBr and KI in water by using the same method as in the previous work[7].

Experimental

Ultra-pure salts of KBr and KI were supplied by Merck. Without further purification, they were dried in an electric oven to a constant weight, the appropriate amount of which was dissolved in conductivity water to give 0.01 N sample solution at 1 atm. The concentration was corrected at each pressure and temperature by means of the P-V-T relation of water just in the same way as that in the previous work.

All the apparatuses and procedures used in the present experiment have been described in detail elsewhere[7].

Consider a glass tube uniform in the internal cross-section (A cm^2) in which a potassium and a cadmium halide solution are contained with the anions common and forms a boundary. When the boundary moves by Δx cm towards the cathode with a constant current i mA passed through the tube Δs seconds, the cation transference number t can be expressed[8] by

$$t = \frac{CA\Delta x F}{i\Delta s},\qquad(1)$$

where F is the Faraday constant and C is the concentration (equiv/l) of the potassium halide solution. The two probe electrodes separated by D cm is here used to detect electrically how far the boundary for moves. The resistance R between the probe electrodes has the following relation[1,7],

$$R = R_1 + \frac{\Delta x}{D}(R_2 - R_1),\qquad(2)$$

where R_1 and R_2 are, respectively, the resistances when the uniform glass column between the probe electrodes is occupied by the potassium halide solution only and when by the cadmium halide solution

5) S.D.Hamann, "Modern Aspects of Electrochemistry", Vol. 9, Chap. 2, ed. by B.E. Conway and J.O'M. Bockris, Plenum, New York-London (1974)
6) K.S.Pribadi, *J. Solution Chem.*, 1, 455 (1972)
7) Y. Matsubara, K. Shimizu and J. Osugi, *This Journal*, 43, 24 (1973)
8) D.A. MacInnes and L.G. Longworth, *Chem. Rev.*, 11, 171 (1932)

only. If we denote $R-R_1$ as ΔR, Eq. (2) can be transformed to the following equation,

$$\Delta x = \frac{D\Delta R}{R_2-R_1}.$$ (3)

Combining Eqs. (1) and (3), we have

$$t = \frac{CADF\Delta R}{i(R_2-R_1)\Delta s}.$$ (4)

The cation transference numbers of KBr and KI in 0.01N aqueous solution at 15, 25 and 40°C up to 1,500 kg/cm² were obtained from Eq. (4) essentially in the same manner as that in an earlier work, and are listed in Table 1.

Discussion

The present result on the cation transference number of KBr at 25°C is compared with that reported by Wall and Berkowitz[2] in Fig. 1. As is shown there, both results agree well at 1 and 1,000 kg/cm². but the literature value at 500 kg/cm² is lower by 0.4% which is only a little smaller than their experimental error 0.6%. Our repeated measurements confirmed that the cation transference number of KBr does not level off in the pressure range of 500 to 1,000 kg/cm², although Horne[9] interpreted the levelling off in favor of his idea on the pressure-induced complete dehydration of ions.

As can be found in Table 1, at all the temperatures studied the cation transference number of KBr decreases with increasing pressure like most of the 1–1 electrolytes reviewed in the introduction. On
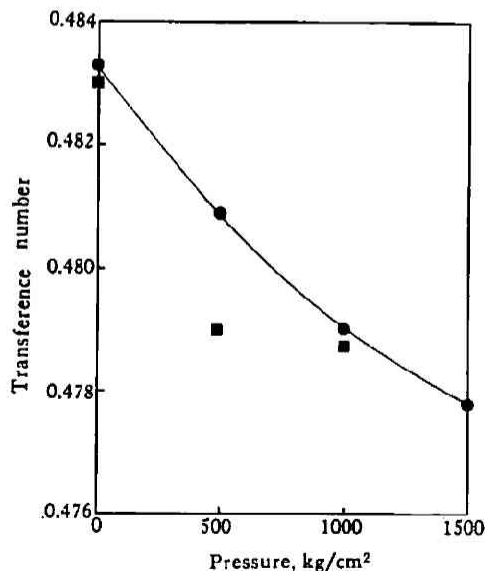

Fig. 1   The cation transference number of KBr at 25°C
●: present work (C=0.01 N at 1 atm)
■: Wall and Berkowitz[2] (C=0.02 N at 1 atm)

10) R.L. Kay and G.A. Vidulich, *J. Phys. Chem.*, **74**, 2718 (1970)

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Table 1   The cation transference numbers of KBr and KI in 0.01 N aqueous solution

Temperature, °C	Pressure, kg/cm²	KBr	KI	KCl*
15	1	0.4862	0.4916	0.4924
	500	0.4829	0.4922	0.4849
	1,000	0.4798	0.4937	0.4815
	1,500	0.4787	0.4972	0.4783
25	1	0.4833	0.4884	0.4901
	500	0.4809	0.4885	0.4861
	1,000	0.4790	0.4913	0.4830
	1,500	0.4778	0.4937	0.4793
40	1	0.4831	0.4873	0.4876
	500	0.4811	0.4877	0.4841
	1,000	0.4792	0.4908	0.4822
	1,500	0.4779	0.4929	0.4802

* from Ref. (7) (at 0.02 N)

the other hand, however, the transference number of KI increases with rise in pressure, apparently like HCl, although there is no similarity in the transport mechanism between potassium ion and proton in strongly hydrogen-bonded water.

In the case of KCl[7], we observed that an increase in temperature reduced the degree of the decrease in the cation transference number with increasing pressure. As we can see in Table 1, the temperature effect on the pressure coefficient of the cation transference number of KBr is somewhat similar to that of KCl, while that of KI is very small. Moreover, under the experimental conditions investigated, the temperature and pressure coefficients of the cation transference number are the same in sign for KBr as found in the case of KCl by Kay et al.[4, 10], but opposite for KI. The symmetric effects of temperature and pressure on the cation transference number of KCl were discussed by Kay et al. as an indication that the structural excess mobility of the potassium ion was greater than that of the chloride ion and the water structure collapsed by the increase in pressure and/or temperature. But the situation seems not so easy to be explained even if we take account of the water structure as well as other factors, because the mobilities of ions are determined by many factors and influenced in a complicated way by temperature and/or pressure. The modified definition of the transference number,

$$t\,(\text{cation}) = \frac{1}{1 + \lambda(\text{anion})/\lambda(\text{cation})}, \qquad (5)$$

tells us that the pressure effect on the transference number can be interpreted by considering relative difference in the pressure effect on the mobility between the cation and the anion. However, in order to discuss the pressure effect on the mobilities of ions in a strict way, the conductivity of the salt must be measured under the same conditions as those in the transference number experiment. For the purpose we are measuring the conductivities of KBr and KI at hight pressures at various temperatures.