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CORRELATION BETWEEN FORMULA WEIGHTS AND ABSOLUTE MOBILITIES OBTAINED BY ISOTACHOPHORESIS FOR ALKYLAMMONIUM AND CARBOXYLATE IONS

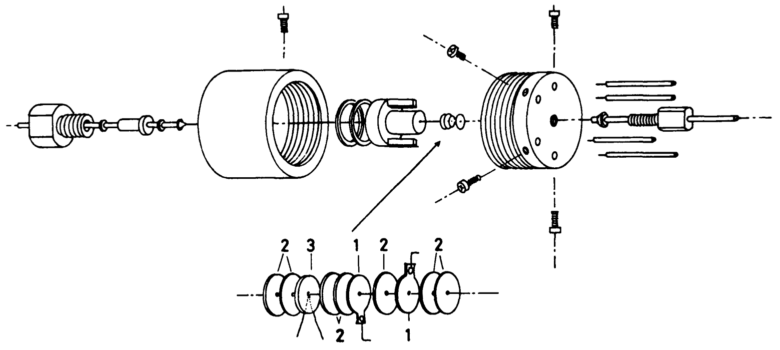
Yoshiyuki KISO and Takeshi HIROKAWA

Applied Physics and Chemistry, Faculty of Engineering, Hiroshima University,
Senda, 3-8-2, Hiroshima 730

Absolute mobilities of n-alkylammonium, mono- and dicarboxylate ions were obtained by means of isotachophoresis. The mobilities were inversely proportional to the square roots of formula weights in the regions of *ca.* 60 to 130, *ca.* 70 to 160 and *ca.* 140 to 200 for the above ions, respectively.

It has been generally accepted that mobilities of ions can be described by Stokes' law, however, many of polyatomic ions deviate from the spherical form and may be regarded as prolate or oblate spheroids. Therefore, the simple hydrodynamic radius in Einstein-Stokes' equation cannot always be adopted for all of ions. In order to overcome this difficulty, many attempts have been made: Elworthy has evaluated the friction coefficients taking into account the spheroidal forms of ions$^{1)}$ and Edward and Waldron-Edward have proposed an empirical formula for evaluation of mobilities taking into account the spheroids and the increment of the Van der Waals radius by additional atoms and functional groups$^{2)}$. However, the estimated values were not in good agreement with the observed ones in spite of taking careful account of several correction factors. On the other hand, Jokl$^{3)}$, Preetz and Blausius$^{4)}$, and Kiso *et al.*$^{5)}$ have shown that a simple correlation may exist between mobilities and formula weights for complex ions and a series of phosphoric acids, although the mobilities have been measured by the method of zone electrophoresis which included considerable uncertainties accompanied by adsorption, electroendosmosis, and difficulty in temperature control. Recently developed isotachophoresis$^{6)}$, which has been used for the separation and analysis of ions with different effective mobilities, was expected to be more reliable in principle for evaluation of absolute mobilities in comparison with zone electrophoresis. The present method may have the following advantages even in comparison with the conductometric method: 1) Mobility of separated ion is obtained individually, 2) only small amount of sample is necessary, 3) several or more samples can be treated at once, 4) in other words, purification of sample is not necessary, and 5) in the aqueous system, purification of water is not necessary.

The isotachophoregram was obtained using a capillary type isotachophoretic analyzer (Shimadzu Seisakusho Ltd., Model IP-1B) equipped with a potential gradient detector (PGD). Since mobilities are sensitive to the change of temperature, the PGD cell was modified in order to measure the temperature of the migrating zones of separated ions during experiments. Figure 1 show a modified PGD cell. The thermo-detector was a polystyrene-molded copper-constantan thermocouple (50μm). The thickness and diameter of a disk were 0.4 and 4.5 mm, respectively, and the



1. Platinum electrodes (4.5mm x 0.1mm)
2. PTFE insulators (4.8mm x 0.1mm)
3. Thermo-detector

Fig. 1. Modified PGD cell.

center of the disk was drilled with a hole (0.5mm ϕ). The conjunctive point of thermocouple was in direct contact with the electrolyte, so as to measure the temperature accurately. The output was connected to a battery-powered digital thermometer (Yokogawa Elec. Co.,Ltd., Type 2575). Particular care was taken for the electric insulation of the cell, thermocouple and thermometer, since even slight leak current caused unstable isotachophoregram. The reading of the thermometer was calibrated against a standard thermometer. The error was within ± 0.2 °C. A switch was added at the electrodes of PGD to short them and adjust null level of the potential gradient on a recorder. The switch was also effective for discharging the remained charges on the capillary system.

The leading and terminating solutions were aqueous imidazole-HCl and L-glutamic acid for the analysis of carboxylates and acetic acid-KOH and ε-aminocaproic acid for alkyl ammoniums. The concentrations of Cl^- and K^+ were 0.005 mol/l and the pH of the leading electrolyte was adjusted to 7.0 and 4.84, respectively, in order to enforce the sample ions being in the full charged state. The length of the capillary tube (0.5mm i.d.) for separation was 20 cm and the applied current was varied in the region of 25 to 50 μA so as not to exceed decomposition voltage at the electrodes of PGD. The voltage applied between the leading and terminating electrodes varied in the region of *ca.* 2 to 4kV at the initial state of migration.

The principle and mathematical treatment of isotachophoresis have been described previously$^{6)}$. It should be noted that the ratio of the potential gradients of the sample or terminating zone (E_V) to the leading zone (E_L), E_V/E_L, is equal to the inverse ratio of the effective mobilities of the separated ions ($\bar{m}_V$) to the leading ion ($\bar{m}_L$);

$$E_V / E_L = \bar{m}_L / \bar{m}_V,$$

where we can obtain E_V/E_L values from the step heights of the recorder traces. The absolute mobilities of K^+ and Cl^- ions have been extensively studied by the conductometric method$^{7)}$ and the temperature dependence of them can be written as;

$$m_0(K^+) = (1.361\ t + 41.701) \times 10^{-5}\ cm^2/Vs$$
$$m_0(Cl^-) = (1.471\ t + 42.301) \times 10^{-5}\ cm^2/Vs,$$

where t denotes the temperature in centigrade. These values were corrected to the effective mobilities at the finite concentration of 0.005 mol/l by the use of Onsager's equation. Then, we can obtain effective mobilities of sample ions $\bar{m}_V$. In order to convert $\bar{m}_V$ to absolute mobility, the calculated ionic strength at the isotachophoretic equilibrium was employed. In practice, a computer program of least-squares method was used for the evaluation of absolute mobility. All calculations were carried out using a computer system HITAC 8700/8800 of Hiroshima University.

All samples were commercial products purchased from Tokyo Kasei Co., Ltd. Imidazole was purified by repeated recrystallization from benzene solution, since slight anionic impurity was found.

The estimation of mobility by the present method seemed reliable taking into account the fact that the obtained absolute mobility of acetate ion well agreed with that obtained by conductometric method. Namely, the extensive works⁷⁾ gave the temperature dependence of absolute mobility of acetate ion as follows;

$$m_0(Ac^-) = (0.800\ t + 22.14) \times 10^{-5}\ cm^2/Vs.$$

This equation gives m_0 at 20.6°C as 38.6×10^{-5} and the value obtained by isotachophoresis was 37.9×10^{-5} cm^2/Vs. The discrepancy was 0.7×10^{-5}, within the experimental error of the present method, $\pm 0.8 \times 10^{-5}$. The error was estimated from the reproducibility for E_V/E_L values of ± *ca.* 0.04.

Table 1 listed the observed E_V/E_L at 21.4 ± 0.5°C, the calculated values of E_V/E_L, pH of zones, concentrations of sample and buffer ions, effective and absolute mobilities for n-alkylammonium ions. Figure 2 shows the correlation between absolute mobilities (m_0) and the inverse of square roots of formula weights ($1/\sqrt{FW}$) for n-alkylammonium ions at 21.4 and 9°C. Figure 3 shows the correlation for mono- and dicarboxylates at 20.6°C. For dicarboxylate ions, the relation of m_0 *vs.* $1/\sqrt{FW/2}$ was also given in order to show the difference of mobilities due to net charges between mono- and dicarboxylate ions. It is apparent that m_0 and $1/\sqrt{FW}$ correlated linearly in the regions of formula weights of 60 to 130 for n-alkylammoniums, 73 to 157 and 144 to 200 for mono- and dicarboxylates, respectively, although the linear correlation was not held for the relatively small ions (FW <60-70). Figure 4 shows the extensive works on the mobilities of alkylammonium ions(7) with the formula weights of 74 to 256 at 25 and 18°C. As expected, the linearity of m_0 *vs.* $1/\sqrt{FW}$ was confirmed. It should be noticed that the linear correlation of primary and secondary ammonium ions differs from that of tertiary

Table 1. Observed E_V/E_L and calculated mobilities of n-alkylammonium ions.

		E_V/E_L								
Ionic species	FW^{a)}	Obsd			Calcd	pH	C_A^{b)}	C_B^{c)}	$\bar{m}$^{d)}	m_0^{e)}
methylammonium	32.1	1.296	1.295	1.294	1.295	4.799	4.489	4.506	52.23	55.0
ethylammonium	46.1	1.601	1.595	1.602	1.599	4.739	4.054	4.073	42.29	44.8
n-propylammonium	60.1	1.929	1.945	1.924	1.933	4.696	3.658	3.679	35.00	37.3
n-butylammonium	74.1	2.067	2.094	2.103	2.088	4.673	3.496	3.517	32.40	34.6
n-amylammonium	88.2	2.223	2.211	2.266	2.233	4.653	3.354	3.376	30.29	32.4
n-hexylammoinium	102.2	2.392	2.347	2.379	2.372	4.633	3.227	3.250	28.51	30.6
n-octylammonium	130.3	2.614	2.632	2.595	2.614	4.600	3.024	3.049	25.88	27.8

a) Formula weights, b) Concentrations of samples (mmol/l), c) Concentrations of buffer (mmol/l), d) Effective mobilities of sample ions ($10^{-5}cm^2/Vs$), and e) Absolute mobilities ($10^{-5}cm^2/Vs$).

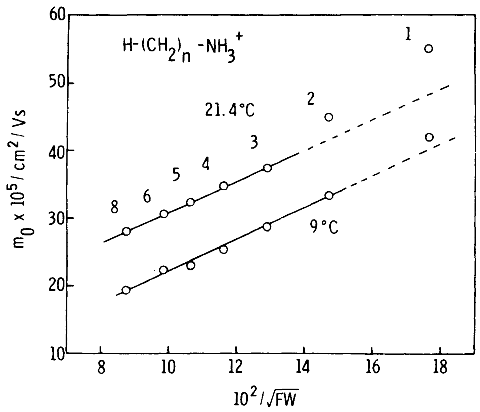


Fig. 2. m_0 *vs.* $1/\sqrt{FW}$ of n-alkylammonium ions.

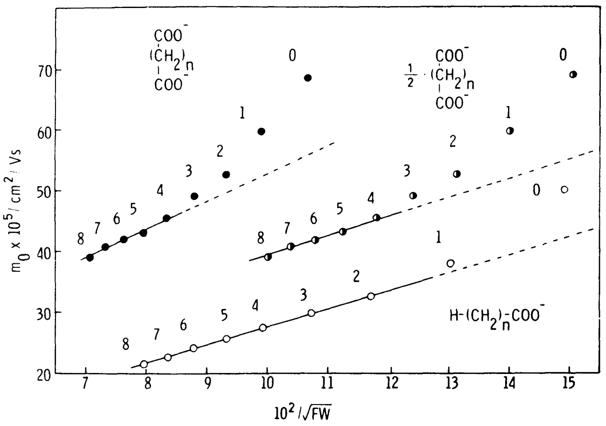


Fig. 3. m_0 *vs.* $1/\sqrt{FW}$ of mono- and dicarboxylate ions (20.6°C).

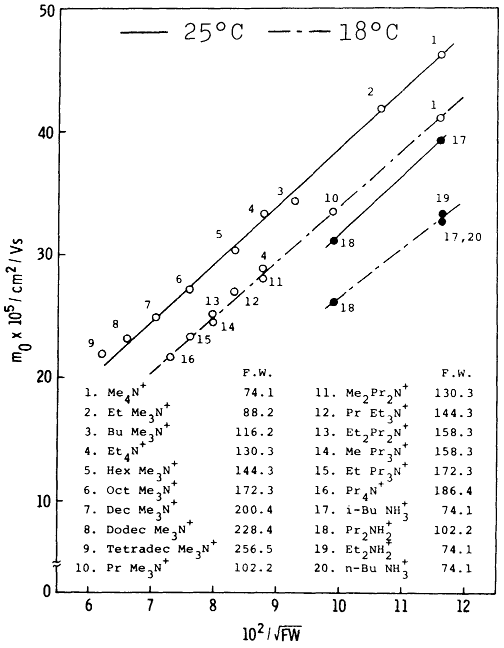


Fig. 4. m_0 *vs.* $1/\sqrt{FW}$ of alkylammonium ions.

and quarternary ammonium ions. These facts suggested that the absolute mobilities of alkylammonium and carboxylate ions can be estimated from the formula weights and their structures. For the larger ions, although the present experiments were limited due to the solubility of samples in water, the use of mixed solvents may afford more detailed relation between m_0 and formula weights and practical equations for evaluation of m_0 of non-spherical ions will be described.

Since the temperature of the present experimental system was governed by a room temperature, more accurate values of m_0 are expected, if it is controlled precisely. Construction of temperature control system for whole capillary system is now in progress and a study on the temperature dependence of mobility is also in progress.

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