

The Behaviour of Weak Electrolytes in Moving Boundary Systems. II. Methodological Investigation of Acetic Acid in Simple Moving Boundary Systems

INGER BRATTSTEN and HARRY SVENSSON

Institutes of Physical Chemistry and Biochemistry, University of Uppsala, Uppsala, Sweden

Right from the time of Kohlrausch there seems to have been a general agreement among the workers in the field of moving boundary electrophoresis—that the electropositive and electronegative radicals (ion constituents) should be regarded as the units of the system. The principles involved in this treatment of a moving boundary system were explicitly discussed by Hartley and Moilliet¹. One consequence is that the mobility of a radical will be a function of the state of equilibrium in which the species is occurring in a certain medium, and it will thus show a variability due to shifts in the ionic equilibria. From the papers of Kohlrausch it is evident that this consequence was realized^{2, 3}. The condition of constant mobilities was introduced only as a device to simplify the mathematical treatment, as is also the case when later theories were proposed on the assumption of constant relative mobilities (Longworth⁴, Svensson^{5, 6}, Dole⁷). The methodological experimental research, which is now mainly serving the purpose to improve and to elucidate the Tiselius' electrophoresis technique of analyzing colloidal mixtures, has been concentrated to the problem of correlating the experimental findings with the available theories, and, in fact, this seems to be the main reason why the restriction of constant relative mobilities is generally adhered to. This condition can be expected to be valid when monovalent strong electrolyte ions are concerned and also in many cases of weak electrolyte systems, when the changes in the state of equilibrium across boundaries are sufficiently depressed.

The accessory constituents in a solution subjected to electrophoresis, the buffer substances, are not yet sufficiently investigated as to their behaviour in moving boundary systems, however, and the purpose of the present investigation

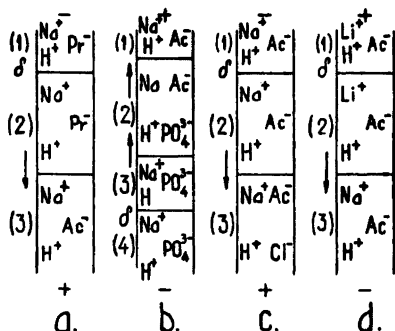


Fig. 1. Schematic representation of the systems investigated. — The stationary boundary is denoted by δ .

is to deal with some typical species of this kind. With this aim, no *a priori* assumptions as to the constancy of the mobilities are needed, or even possible; the variation of this function is instead being investigated. It is then immediately evident that the extended theories are not necessarily applicable, but the moving boundary equation, which does not involve any approximation and no assumption of constant mobilities, should be adequate to describe the mass transport of the constituents across boundaries. This equation is used here in the symmetrical form given by Svensson ⁶:

$$\frac{c_{ij} (u_{ij} - U'_j)}{\kappa_j} = \frac{c_{i,j+1} (u_{i,j+1} - U''_j)}{\kappa_{j+1}} \quad (1)$$

where c is the concentration of the constituent, and u its mobility. U' and U'' are the velocities of the boundaries divided by the field strengths above and below it, respectively; they have the dimensions of a mobility and may be called the mobilities of the boundary. κ is the conductivity. The first subscript, i , denotes the number of the constituent, the second, j , the number of the boundary and the number of the inter-boundary layer. The quantities U' and U'' are related to the velocity of the boundary, V , in cm per sec, by the equations

$$V_j = \frac{U'_j I}{\kappa_j} = \frac{U''_j I}{\kappa_{j+1}} \quad (2)$$

where I is the current density.

The concentration unit inserted in equation (1) was millimol per liter in this investigation.

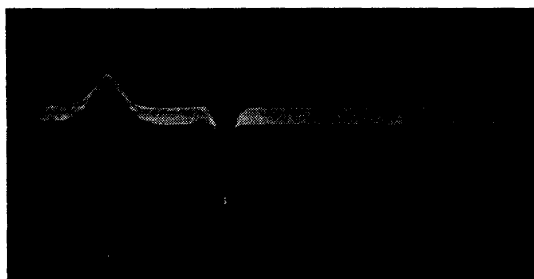


Fig. 2. Optical pattern of an acetate-propionate experiment arranged according to Fig. 1 a. The current direction is from right to left.

The mass transport of acetic acid was investigated in some simple moving boundary systems. With the aid of experimentally determined quantities it was tested if the transfer took place according to the moving boundary equation under the experimental conditions. Three different types of experiments were performed.

System 1

The original boundary was formed between a solution (1) of sodium propionate and propionic acid and a solution (3) containing sodium acetate and acetic acid. On passage of current, the system indicated in Fig. 1 a developed in the negative limb. Analyses showed that the acetate radical disappeared completely in the boundary and the original acetate solution was followed by an adjusted propionate solution. Thus both the negative radicals disappeared in the moving boundary, and the moving boundary equation, applied to each of them, will give the mobilities of these constituents, for the propionate radical in solution (2), and for the acetate radical in solution (3). Just as we are accustomed to find in the case of colloids in electrophoresis, the mobility of the acetate radical depends on the pH of the solution, attaining low values when there is much free acid in excess, and approximating to that of the free acetate ion when the degree of dissociation is increased. It is evident that this type of experiment is useful to obtain the mobility of a radical in a certain medium, and it was used for this purpose in the further work. The conditions influencing the properties of the adjusted solution were investigated in some detail, and it was found sufficient to keep solution (1) enough dilute to ensure a gravitationally stable stationary boundary. The composition of solution (2) was determined by the properties of solution (3) exclusively, to within the experimental errors. Propionic acid was chosen as the indicator radical because it was expected to be slower than the acetate radical, which was confirmed by the experiment. Although gravitationally stable, however,

the resulting system showed an inverted gradient curve, indicating that the propionate solution (2) was optically denser than the acetate solution (3), Fig. 2.

System 2

Another type of system is obtained if the experiment is arranged as indicated in Fig. 1 b. The top solution (1) consisted of an acetate buffer of pH 4.90, the bottom solution (4) was a phosphate buffer of pH 6.80. Sodium ions made the positive constituent. On passage of current, two ascending boundaries developed in the positive limb; they remained sharp during the experiment. Analyses of the liquid layers gave the distribution of the constituents shown in Fig. 1 b. Thus solution (2) contained both the acetate and the phosphate radicals. From the velocity of the boundary (1) we can calculate the mobility of the phosphate radical, and from the velocity of the boundary (2) we obtain the mobility of the acetate radical. Both these mobilities refer to the state of solution (2), which is developed during the experiment and thus of unknown composition. Therefore, from this kind of experiment no mobility can be obtained referring to a solution of initially known composition. For the purpose of mobility determinations, this type of experiment is generally not as useful as that previously described.

The acetic acid is present on both sides of the boundary (1). In solution (1), the composition is known, and the mobility of the acetate radical can easily be determined experimentally; in solution (2) the composition can be determined analytically on an isolated sample, and the mobility of the acetate radical in this solution is that obtained from the boundary (2). If the conductivity of both solutions are measured, enough data are known to allow the transport of acetic acid across the phosphate boundary (1) to be calculated and checked with the requirements of the moving boundary equation.

It is obvious that the difference in behaviour of the acetate radical in the systems 1 and 2 is caused by the difference in mobility and acidity of the two indicator substances, propionic acid and phosphoric acid. The same phenomenon was observed and investigated by Alberty and Nichol⁸ in independent research.

System 3

With the experiments arranged according to Fig. 1 c, a system was obtained which also contained the acetate radical in all liquid layers. Here the descending boundary in the negative limb was a chloride boundary, or, in some instances, a perchlorate boundary. The initial boundary was

formed between a solution (1) containing sodium acetate and acetic acid, and a solution (3) containing these substances and, in addition, sodium chloride (sodium perchlorate). The transfer of substance across the stationary boundary was not investigated; the absolute composition of solution (1) is therefore not of interest for the work. It was kept at the same relative concentration as the adjusted solution (2), but somewhat more dilute, to ensure gravitational stability. The adjusted solution (2) was isolated and analyzed after the experiment. After the conductivities of the solutions (2) and (3) had been measured, the quantities U' and U'' were computed from the boundary velocity. The mobilities of the acetate radical in the solutions (2) and (3) were determined in separate experiments, and since the composition of solution (3) was known, the transport of the acetate radical across the boundary (2) could be calculated.

EXPERIMENTAL

The electrophoresis apparatus used was of the type delivered by LKB-Produkter Fabriks-AB, Stockholm. Observations were made with the cylindrical lens method (Svensson ⁶). The current was read on a calibrated precision milliammeter. As the peaks were of constant sharpness throughout the runs, direct reading of the cell coordinate and plotting against time proved to give satisfactory results. The electrodes were silver plates coated with silver chloride and surrounded by one-molar sodium chloride. The volume correction on the mobilities (MacInnes and Longworth ⁹) was not carried out, thus the mobilities refer to the apparatus as the plane of reference. All experiments were carried out at 0° C.

In the course of the investigation it turned out that certain disturbances, such as anomalous conductivity values of the adjusted solutions, the presence of foreign ions in the U-tube after the experiment, steadily increasing current, *etc.*, were caused by convections in the electrode tubes. These convections may have different origin, heat convection, electro-osmotic streaming at the glass wall, and convections due to the formation of gravitationally unstable moving boundaries. These effects were avoided by using packings of some kind, such as cotton or paper pulp, in the electrode vessels. In order to prevent a net transport of liquid through the U-tube due to the increased electro-osmosis, the apparatus was kept closed during the run.

The chemicals used were of analytical grade. The distilled water usually showed a conductivity of $2 \cdot 10^{-6}$ ohm⁻¹ cm⁻¹ and was not further purified. The sodium chloride was recrystallized from water. The solutions used in the experiments were prepared from stock solutions kept in alkali-resistant glass bottles with equipment to exclude the carbon dioxide in the air. Common analytical methods were used in the standardizations; sodium chloride was determined by weighing, the acids and the bases acidimetrically.

In the experiments of system 2, the analyses of the adjusted solutions (2) involved the determination of phosphoric acid and acetic acid. The former acid was determined by the volumetric molybdate method, the later by steam distillation of the samples after addition of concentrated sulfuric acid and MgSO₄. The distillate was then titrated with standard base. Usually the values obtained by this method were a little low, and the concentration of acetic acid was therefore also computed indirectly from the analytical

data for phosphoric acid and total acidity, after the concentration of the sodium ion constituent was calculated by means of the moving boundary equation.

The adjusted solutions isolated in the experiments belonging to system 3 were analyzed as follows. First, the conductivity was measured. Second, neutralization by standard base gave the amount of free acid. The neutralized solution was evaporated with sulfuric acid, ignited, and weighed. A small correction had to be applied for impurities, mainly from the standard base used in the neutralization. It was therefore necessary to run a blank; with these corrections applied, the analyses were generally reproducible to within 0.5 %.

All concentrations were determined in mols per liter at room temperature. The concentrations at 0° C were calculated from these data, and are given in the tables, where mC means milli-molar.

THE MOBILITY MEASUREMENTS

The main purpose of this work was to investigate the transfer of acetic acid, but in the course of the work it turned out necessary to make systematical determinations of the mobilities of the remaining constituents also. Due to a comparatively great spreading of the experimental material, it was advantageous to collect and to compare the results from similar experiments in order to level the data. This spreading was in many instances caused by imperfections in the experimental outfit. The special top cell with enclosed electrode tubes designed by Longsworth¹⁰ for precision mobility measurements was not available to us in this investigation.

Thus the mobility values of the chloride ion were collected from the experiments according to system 3, where this constituent disappeared in the boundary.

The mobilities of the acetate radical at different pH:ses and ionic strengths were derived from experiments according to system 1.

The mobility of the sodium ion was determined in experiments arranged according to Fig. 1 d. A moving boundary system was formed between solution (1) containing a mixture of lithium acetate and acetic acid and solution (3) containing a mixture of sodium acetate and acetic acid of the desired pH and ionic strength. A moving boundary between Li^+ and Na^+ was formed, which remained sharp on the descending (positive) side.

The experiments were performed with rather dilute solutions and within a limited concentration range, 30—60 mC. Evidence from the conductivity measurements in comparison with the experimental mobilities of the constituents showed that the degree of interaction could be approximately treated as an unspecific ionic strength effect, in addition to the specific interaction between the H^+ and the Ac^- radicals. Therefore, the mobilities were determined as functions of the ionic strength, and additivity was assumed.

Thus the mobilities of the Na^+ ion and of the free acetate ions were regarded as independent of the presence or absence of chloride provided that the ionic strength was the same. A direct determination of the mobility of Ac^- in solution (3) of system 3 could not easily be done due to the fact that the chloride ion is faster than the acetate radical. If Cl^- were present in the system, it would therefore be expected to give rise to a boundary migrating in front of the acetate boundary, and the mobility to be obtained for the acetate radical would refer to another medium than the original solution.

The mobilities of the free acetate ions were obtained from the experimental measurements of the mobilities of the radical. If we denote the mobility of the radical by u and the mobility of the corresponding free ion by v , we have for a monovalent weak acid or base:

$$u = \alpha \cdot v \quad (3)$$

where α is the degree of dissociation. In this procedure, the influence on the mobilities of varying concentration of free acetic acid was neglected. This was allowed since the absolute differences in the amounts of free acid were only slight. The conclusion was confirmed by conductivity measurements on the mixtures.

The ionic mobilities were plotted against the square root of the ionic strength, and straight lines were drawn originating from the known values of the limiting mobilities. The extension of the square root law to these concentrations involves a certain error, but the procedure was found to give satisfactory results for the present purpose.

The mobility values to be inserted in the moving boundary equation were taken from the plots, except in the case of experiment 7 of Table 8, which contained phosphoric acid. For this radical no extensive mobility determinations were available, and the invariant of the equation was calculated with the aid of the primary experimental data.

RESULTS

The experimental material is collected in the Tables 1—8. The values of the limiting mobilities of the ions were obtained from Landolt-Börnstein, Tabellen, or from International Critical Tables.

The experimental mobilities of Cl^- are given in Table 1. They were plotted against the square root of the ionic strength, and a straight line originating from the known limiting mobility, $-42.8 \cdot 10^{-5}$, was drawn. The leveled data obtained from this line are given in the last column of Table 1.

Table 1. The mobility of Cl^- in acetate solutions at $0^\circ C$.

Exp.	Concentration, mC			Mobility $\cdot 10^5$	
	Na^+	Cl^-	Ac^-	exp.	from Diagram
1	35.10	14.98	30.50	— 38.82	— 38.68
2	35.00	14.98	30.50	— 39.06	
3	35.00	14.98	30.50	— 39.03	
4	40.20	15.20	30.52	— 38.33	— 38.40
5	40.20	15.20	30.52	— 38.51	
6	40.20	15.20	30.52	— 38.31	
7	40.20	15.20	30.52	— 38.31	
8	40.20	15.20	30.52	— 38.39	
9	40.20	15.20	30.52	— 38.34	
10	45.4	29.97	40.38	— 38.66	— 38.14
11	45.4	29.95	40.38	— 38.78	
12	45.4	29.95	40.38	— 37.27	
13	45.4	29.95	40.38	— 37.90	
14	45.4	30.00	40.38	— 37.48	
15	61.7	30.04	40.00	— 37.24	— 37.33
16	64.5	50.0	15.25	— 37.42	— 37.25
17	64.9	50.0	15.25	— 37.43	— 37.25
18	64.9	50.0	15.25	— 36.95	
19	64.9	50.0	15.25	— 37.32	

The mobilities of Na^+ are given in Table 2. Its limiting mobility was put = $26.42 \cdot 10^{-5}$.

Table 3 gives the mobility data obtained for the acetate radical. The v values obtained according to equation (3) were plotted against the square root of the ionic strength, and the leveled mobilities are introduced into Table 3, column 9. The limiting mobility of the acetate ion was put = $-21.04 \cdot 10^{-5}$.

Table 2. The mobility of Na^+ in acetate solutions at $0^\circ C$.

Exp.	Concentration, mC		Mobility $\cdot 10^5$	
	Na^+	Ac^-	exp.	from Diagram
1	30.20	35.46	24.08	24.02
2	30.20	40.36	24.05	
3	62.7	78.4	22.96	22.97
4	62.7	73.0	23.00	

Table 3. The mobility of the acetate radical at 0° C.

Exp.	Concentration, mC		$\alpha \cdot 10^2$	Mobility $\cdot 10^5$		
	Na ⁺	Ac ⁻		u	v	v from Diagram
1	30.18	40.36	74.8	- 14.16	- 18.94	- 18.65
2	30.18	35.46	85.1	- 16.12	- 18.95	
3	30.18	35.46	85.1	- 15.80	- 18.51	
4	35.20	49.9	70.5	- 13.10	- 18.58	- 18.43
5	40.20	68.5	58.9	- 10.61	- 18.00	- 18.26
6	40.25	47.0	85.6	- 15.62	- 18.24	
7	40.20	47.1	85.3	- 15.43	- 18.08	
8	50.3	71.0	71.0	- 12.54	- 17.67	- 17.91
9	54.8	111.3	49.2	- 8.80	- 17.78	- 17.75
10	54.8	68.3	80.2	- 14.30	- 17.82	
11	54.8	60.7	90.4	- 16.06	- 17.80	
12	63.0	75.8	83.0	- 14.37	- 17.31	- 17.49
13	62.9	78.4	80.1	- 14.30	- 17.84	
14	63.0	126.9	49.6	- 8.91	- 17.95	
15	63.0	86.1	73.1	- 12.81	- 17.51	

Table 4. The mobility of ClO_4^- from moving boundary experiments.

Exp.	Concentration, mC			Mobility $\cdot 10^5$	
	Na ⁺	ClO_4^-	Ac ⁻	exp.	from Diagram
1	53.8	21.56	40.45	- 33.84	- 33.74
2	53.8	21.56	40.45	- 34.14	
3	53.8	21.56	40.45	- 33.86	

Table 5. The mobility of ClO_4^- in water solutions of NaClO_4 from conductivity measurements.

$\mu \cdot 10^3$	$\kappa \cdot 10^3$	$(\kappa/\text{Fc}) \cdot 10^5$	$(\kappa/\text{Fc}) \cdot 10^5$ from Diagram	$u_{\text{Na}^+} \cdot 10^5$ from Table 2	$u_{\text{ClO}_4^-} \cdot 10^5$
27.12	1.541	58.90	59.19	24.15	- 35.04
43.33	2.407	57.55	57.65	23.53	- 34.12
54.3	2.983	56.93	56.84	23.18	- 33.66
54.4	2.996	57.11		23.18	

Table 6. The conductivity of sodium acetate-acetic acid solutions at 0° C.

a. Experimental.

Concentration, mC		$\kappa \cdot 10^3$
Na ⁺	Ac ⁻	
20.12	23.05	0.851
30.20	35.45	1.247
30.20	40.57	1.242
30.20	31.23	1.245
35.32	50.0	1.441
40.25	80.0	1.620
40.25	47.1	1.620
40.25	68.2	1.625
40.30	47.0	1.624
40.30	42.09	1.629
45.2	60.8	1.828
50.4	70.9	2.010
50.3	58.6	1.955
50.3	51.0	1.917
54.8	68.2	2.169
55.1	60.9	2.181
62.9	78.1	2.468
63.0	126.8	2.458
63.0	86.1	2.468
70.2	80.9	2.702

b. Calculated from experimentally determined ionic mobilities.

$\kappa \cdot 10^3$	$u_{\text{Na}^+} \cdot 10^5$	$u_{\text{Ac}^-} \cdot 10^5$	$(u_{\text{Na}^+} - u_{\text{Ac}^-}) \cdot 10^5$	$\kappa \cdot 10^3$	
				calc.	from Table 6 a
30	24.04	- 18.64	42.68	1.236	1.237
40	23.65	- 18.26	41.91	1.617	1.620
50	23.32	- 17.90	41.22	1.989	1.990
60	22.96	- 17.58	40.54	2.347	2.350

For the perchlorate ion, only a few experimental mobilities were available, Table 4, but they were supplemented by mobilities computed from the conductivities of sodium perchlorate solutions. The latter data are collected in Table 5. In the third column, we have the observed conductivities, in the

Table 7. The conductivity of NaCl.

Comparison between values obtained in different ways.

Column 1: Mobility of Na^+ from Table 2.

Column 2: Mobility of Cl^- from Table 1.

Column 3: The sum of 1 and 2.

Column 4: The same sum calculated from experimentally determined conductivities.

Column 5: The same sum from *International Critical Tables* (equivalent conductivities).

$\mu \cdot 10^3$	1	2	3	4	5
30	24.0	39.0	63.0	63.0	63.0
40	23.65	38.4	62.05	62.05	62.3
50	23.32	37.85	61.2	61.2	61.7
60	22.99	37.4	60.4	60.5	61.2

fourth they have been divided by the Faraday constant. These values were plotted against the square root of the ionic strength, the limiting value of $u_{\text{Na}^+} + |u_{\text{ClO}_4^-}|$ being put = $64.6 \cdot 10^{-5}$. The levelled data from the line are introduced into column 5. Corresponding values for Na^+ are found in column 6, and in column 7 the mobilities of the perchlorate ion have been computed by difference.

A valuable guide in drawing the straight lines was obtained from the requirement that the added mobilities of any pair of cation and anion must check reasonably with the conductivity of the corresponding salt. The straight lines were adjusted until this condition was fulfilled. Primary conductivity data for the adjusted acetate solutions are given in Table 6 a, and those calculated from the mobilities of Na^+ and Ac^- in Table 6 b. The experimental data were plotted against the ionic strength, and in the last column of Table 6 b interpolated conductivity values taken from this plot are given for comparison with the calculated values. Table 7 gives a comparison between values of κ/Fc for NaCl solutions obtained from the sum of u_{Na^+} and $|u_{\text{Cl}^-}|$, from direct conductivity measurements, and from *International Critical Tables*.

The tables now commented upon give us all data necessary for testing the moving boundary equation for both Na^+ and Ac^- , which constituents are present on both sides of the moving boundary. The final calculation is carried out in Table 8.

The first column is the number of the experiment. Each figure denotes an average of at least three determinations. It was generally found that more reproducible results were obtained for the concentrations than for the mobil-

Table 8. The validity of the moving boundary equation for Na^+ and Ac^- .

1	2	3	4	5			8	9	10		11		12	13	14		15	16		17
				NaCl	HAc	NaOH			$-v_{\text{Ac}^-}$	$-u_{\text{Ac}^-}$	Mobilities $\cdot 10^5$	exp.			calc.	$-U \cdot 10^5$		Na^+	Ac^-	
Exp.	j	pH	$\mu \cdot 10^3$	Concentration, mC			$a \cdot 10^2$	c_{HAc}					u_{Na^+}	$\kappa \cdot 10^3$						
1	2		30.0	0.00	40.85	30.02	73.5	10.82	18.64	13.70	23.98	1.247	28.31	1.258	4.79					
	3		35.0	14.98	30.50	19.94	65.4	10.55	18.45	12.06	23.78	1.704	38.68	1.284	4.77					
2	2		35.8	0.00	41.07	35.78	87.1	5.30	18.40	16.03	23.76	1.450	29.20	1.304	3.73					
	3		40.2	15.00	30.52	25.21	82.6	5.31	18.25	15.08	23.60	1.907	38.40	1.307	3.73					
3	2	4.82	35.25	0.00	61.2	35.25	57.6	24.95	18.47	10.64	23.78	1.444	23.06	1.144	5.26					
	3	4.41	45.5	29.97	40.38	15.51	38.4	24.87	18.07	6.94	23.43	2.388	38.14	1.170	5.28					
4	2		51.0	0.00	60.9	51.0	84.5	9.43	17.80	15.00	23.25	1.995	24.82	1.230	3.05					
	3		61.8	30.04	39.95	31.74	79.5	8.19	17.54	13.95	23.02	2.990	37.33	1.247	3.12					
5	2	6.18	49.4	0.00	50.9	49.4	96.5	1.78	17.91	17.30	23.30	1.924	20.71	1.131	9.02					
	3	6.09	64.5	50.0	15.25	14.54	95.3	0.72	17.45	16.63	22.98	3.461	37.25	1.120	9.06					
6	2		47.9	NaClO_4																
	3		53.8	0.00	55.9	47.9	85.7	7.99	17.95	15.38	23.45	1.915	26.39	1.248	3.22					
7	1	4.90	35.0	NaH_2PO_4																
	2	4.43	31.4	0.00	55.0	35.0	63.6	20.0	18.45	11.63	23.82	1.423	15.94		1.627					
				20.5	29.0	10.9	37.6	18.1	18.6	6.99	24.0	1.223	13.77		1.607					

ities. In the experiments recorded here, the maximum deviation between the individual determinations never exceeded 1 %. The experiments 1—6 belong to the type of system 3; experiment no. 7 belongs to the type of system 2.

The second column of Table 8 gives the number of the liquid layer, $j = 1$ for the top solution, $j = 2$ for the adjusted solution, *etc.*, according to Fig. 1. Column 3 gives the pH. The columns 4—7 give the ionic strength and the concentrations of the components in the solutions; for greater convenience, we have given these concentrations rather than those of the electrical constituents, which are of course Na^+ , H^+ , Ac^- , Cl^- , ClO_4^- , and PO_4^{3-} . Column 8 gives the degree of dissociation; for this acid it can be put equal to the ratio between the concentration of sodium acetate and the added concentrations of acetate and free acid. Column 9 gives the concentration of free acetic acid present. In the columns 10—12, we find the mobilities of Na^+ , derived from Table 2, that of the acetate ion derived from Table 3, and that of the acetate radical computed from equation (3). The experimentally found and the computed conductivities are given in the columns 13 and 14, and the quantities U' and U'' defined by equation (2) in column 15. The last two columns give the values of $c(u-U)/\kappa$, claimed to be an invariant by the moving boundary equation.

The constancy of this function is well within the experimental errors in all instances. In the case of ion species of the sodium type, the validity of the moving boundary equation was shown by Longworth (1945¹¹, and previously), and the experiments reported here show that also the transport of a typical weak acid such as acetic acid is adequately described by the equation.

DISCUSSION

Column 8 of Table 8 is interesting because it shows that the concentration of free acid is very nearly unchanged across the moving boundary in the experiments 1—3 belonging to system 3. In a recent investigation by Longworth¹², where the electrophoretic behaviour of some typical protein systems was computed with the aid of Dole's theory and compared with experiments, this condition was assumed to prevail in the system discussed. It was pointed out that it is possible in such a case to regard the undissociated portion of the acid as part of a mixed solvent, and to treat the ionic form as an independent constituent of the strong electrolyte type. Such a mode of treatment would allow the assumption of constant relative mobilities to be extended to this constituent. With the aid of the concentration change of the free acetate ions, calculated on these assumptions, the pH change across the boundary was computed, and a correction applied for the corresponding change in the mobility of the protein, which is a pH function. Thus the procedure was used

to improve the results obtained with the aid of the theory by taking into account deviations from the relative constancy of the mobilities in different ways for the simple acid and for the protein. It is evident, however, that this mode of treatment of a monovalent acid must be regarded as a special case, although it may be frequently met with in electrophoresis. Only a sufficient knowledge of the course of the equilibrium reactions in the boundary makes it possible to decide whether it is permissible or not. In the remaining experiments of the same kind (system 3) in Table 8, and in experiment 7, where the concentration distribution across an ascending phosphate boundary is investigated, the assumption of constant concentration of free HAc across the boundary is still a rather good approximation, but there are certain deviations that may be greater than the experimental errors. If the invariant of the moving boundary equation is computed for the free acid in these cases, the agreement is not satisfactory.

In the type of experiments described as system 1, all the free acetic acid is transferred into the ionic form in the boundary. In this case, it is therefore not possible to regard the two forms of acetic acid independently, and nor is this a possible way when more complicated substances are concerned. This was expressed in a generalized form by Hartley and Moilliet¹ who made the statement that it is important to distinguish between quantities pertaining to the radical, which are open to direct measurements, and quantities pertaining to the ionized forms of a radical, which depend upon a knowledge of the degree and manner of the dissociation. Only if we regard the mass transport of the radical from one homogeneous liquid layer to the adjacent one is it possible to avoid a consideration of the particular paths of the reactions in the boundary. But if we adopt this treatment, no possibilities are left to make any general assumptions as to the constancy of the mobilities. In general, these quantities must be determined experimentally as functions of the state of the solutions under investigation. In the experiments reported here, the laws of dilute solutions could be used to simplify the evaluation of the mobilities. In the type of systems generally met with in practice, however, the state of the interaction between the constituents is rather complex. Some further experiments, which stress this feature, will be reported in a following paper.

SUMMARY

The behaviour of acetic acid in some 3-component moving boundary systems was studied. With an acetate buffer placed below a propionate buffer, a sharp descending boundary was obtained in which both radicals disappeared. These boundaries can be used for measuring the mobilities of the radicals

under widely varying conditions (pH, ionic strength, etc.). — With a phosphate buffer placed below an acetate buffer, two sharp ascending boundaries appeared, the solution between them being a mixed zone containing both the acetate and the phosphate radicals. — In experiments where acetic acid was present on both sides of a moving boundary, the concentration distribution of the acetate radical was found to be in accordance with the moving boundary equation.

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