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DETERMINATION OF ABSOLUTE MOBILITIES AND p*K* VALUES BY ISOTACHOPHORESIS

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SUMMARY

Once the steady state has been reached in isotachophoresis, all sample zones have a particular conductivity for a given operational system. With a computer program all combinations of absolute mobilities and p*K* values can be calculated to give a well-defined zone conductivity for a given electrolyte system. If these absolute mobilities are plotted as a function of their p*K* values, a relationship is obtained that we call an isoconductor.

Isoconductors of different electrolyte systems will intersect. By measuring the step-heights of an ionic species in two different electrolyte systems and by converting these step-heights into zone conductivities, the absolute mobility and p*K* value of that ionic species can be obtained from the intersection of the two isoconductors concerned.

Both in a graphic and computational way, we have determined the absolute mobilities and p*K* values for some monovalent acids with this method. The results show a great similarity with values available in literature.

INTRODUCTION

The choice of an electrolyte system plays an important role when using isotachophoresis (ITP) as a separation technique. In ref. 1 a chapter has already been dedicated to the use of differences in mobilities and p*K* values to separate a mixture into its components. Also a computer program has been described with which an optimal choice of an electrolyte system can be made, provided that all mobilities and p*K* values of the sample ionic species are known. However, this often causes a problem as mobilities and p*K* values are not always available in the literature, especially if amphiprotic ionic species are considered.

This paper describes a method for the determination of absolute mobilities and p*K* values of monovalent ionic species from two step-heights measured in two different electrolyte systems.

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THEORETICAL

A step-height measured in an ITP separation (determined with a conductivity–potential gradient detector or with a thermocouple–thermistor) is linked to a fixed conductivity in the zone concerned. Ionic species are identified by these step-heights in ITP. However, such a step-height can stand for a whole series of ionic species, because all the ionic species that show the conductivity concerned, as a result of a particular absolute mobility and p*K* value, show the same step-height. This is the reason why absolute mobilities and p*K* values of ionic species cannot be obtained from a step-height.

With a computer program* all combinations of absolute mobilities and p*K* values can be calculated to give a well-defined zone conductivity for a given electrolyte system. If these absolute mobilities are plotted as a function of their associated p*K* values, a relationship is obtained that we call an isoconductor. Consequently, an isoconductor can be defined as the set of all ionic species (indicated by the quantities on the axis of the graph) having one and the same zone-conductivity (zone temperature, electric field strength) in an ITP operational electrolyte system. Fig. 1 shows such an isoconductor with a conductivity of 0.6, for an anionic separation in an electrolyte system with a pH in the leading zone (pH_L) of 6.02. The course of this isoconductor is clear. At a pH_L of 6.02, the pHs in the sample zones will also be *ca.*

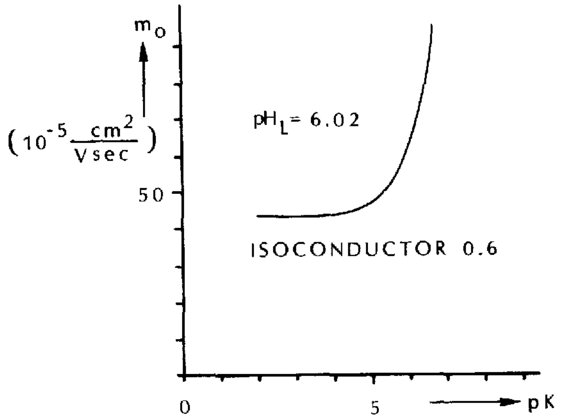

Fig. 1. The relationship between absolute mobilities and p*K* values of ionic species, which show one and the same zone conductivity in a given ITP electrolyte system, is called an isoconductor. In this figure the isoconductor with a value of 0.6 is shown for an electrolyte system at a pH_L of 6.02 (for further conditions see Table I).

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* Refs. 1 and 2 describe a computer program by which, for a given isotachophoresis electrolyte system, all quantities, including the zone conductivities, can be calculated from absolute mobilities and p*K* values of the ionic species. In this program all p*K* values and all absolute mobilities are needed for all ionic species. The influence of buffering ionic species and solvent ions are taken into account, especially for calculations at low p*K* values. This program works in a similar way, on understanding that first a p*K* value is assumed, for which zone conductivities are calculated for a low and a high absolute mobility. By an iteration procedure between these mobilities, that mobility can be found with which the requested zone conductivity is given.

6, which means that all ionic species with p*K* values up to *ca.* 4.5 will be practically fully ionised. So all these ionic species must have one and the same absolute mobility in order to show the same conductivity.

At p*K* values higher than *ca.* 4.5 the degree of ionisation decreases, hence the absolute mobilities must increase to conform to the conductivity desired. If we measure the step-height of an ionic species belonging to an isoconductor value of 0.6 at a pH_L of 6.02, in another electrolyte system of a pH_L of 7.05, for example, this will have a different value.

In general this means a larger conductivity in its zone as ionic species will be more fully ionised at higher pH values, showing larger effective mobilities. Of course other factors such as the mobility of the counter-ionic species, play an important part.

Let us assume that the step-height at a pH_L of 7.05 correlates with a zone conductivity of 0.8. In Fig. 2 the isoconductors with values of 0.6 (pH_L = 6.02) and 0.8 (pH_L = 7.05) have been plotted: note that they intersect. From this point of intersection the absolute mobility and p*K* value of that ionic species, that comes up to the zone conductivities of the two isoconductors, can be found. In this way we can determine the absolute mobilities and p*K* values of ionic species from the intersections of two isoconductors by measuring two step-heights (zone conductivities) in two different electrolyte systems.

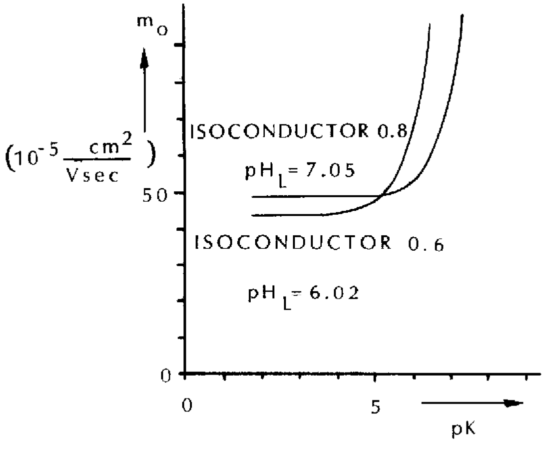


Fig. 2. Isoconductors with values of 0.6 (pH_L = 6.02) and 0.8 (pH_L = 7.05) cut each other. An ionic species that comes up to both isoconductor values must have an absolute mobility and p*K* value conforming to the values of the intersection of the two isoconductors.

Of course, the absolute mobility can be read directly from one isoconductor if the p*K* value of an ionic species is exactly known or if the isoconductors do not intersect.

For the calculation of the intersections of isoconductors we also used a computer program (see Fig. 3).

In this case the two electrolyte systems must be well chosen as not all isoconductors cut each other (see Fig. 4). Fig. 4 shows some isoconductors for electrolyte

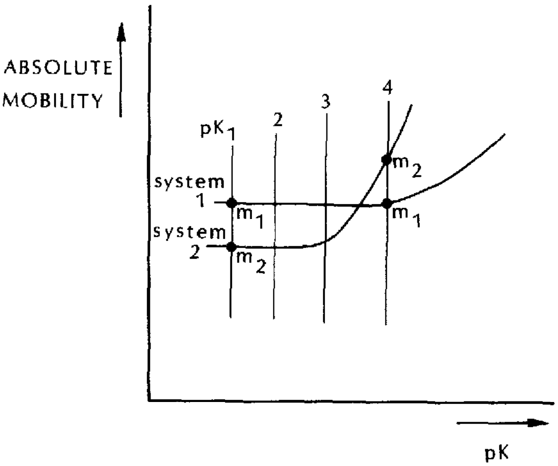


Fig. 3. The principle of the computer program for the calculation of the intersection of two isoconductors is as follows. For both the electrolyte systems 1 and 2, the absolute mobilities ($m_1 > m_2$) are calculated, conforming to the isoconductors concerned at pK_1. This is repeated for larger pK values (pK_2 and pK_3), until the mobility m_2 is larger than m_1 (at pK_4). The intersection of the two isoconductors can be found by iterating between the pK values pK_3 and pK_4.

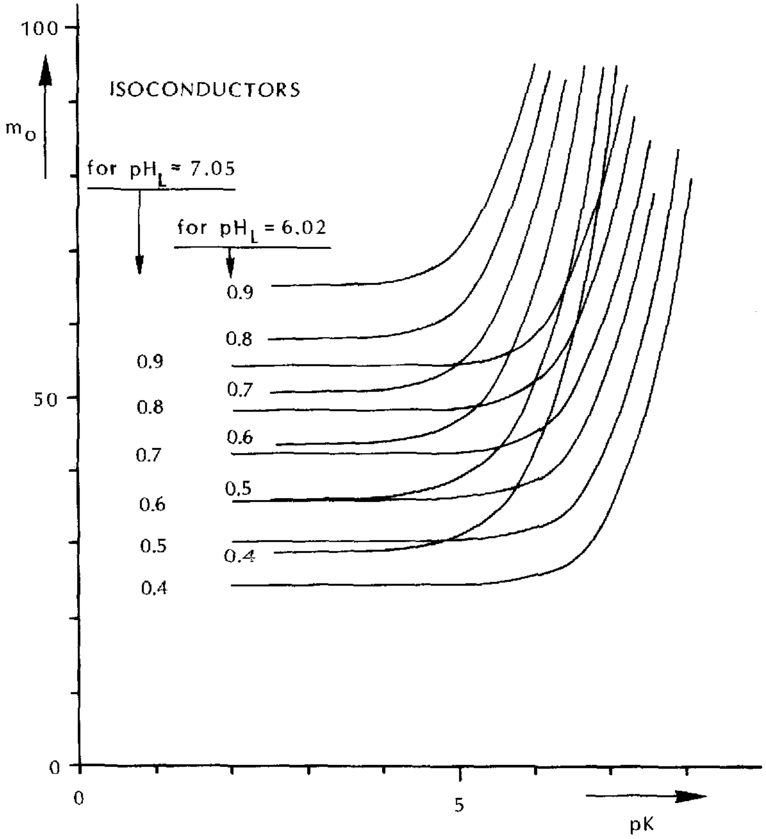


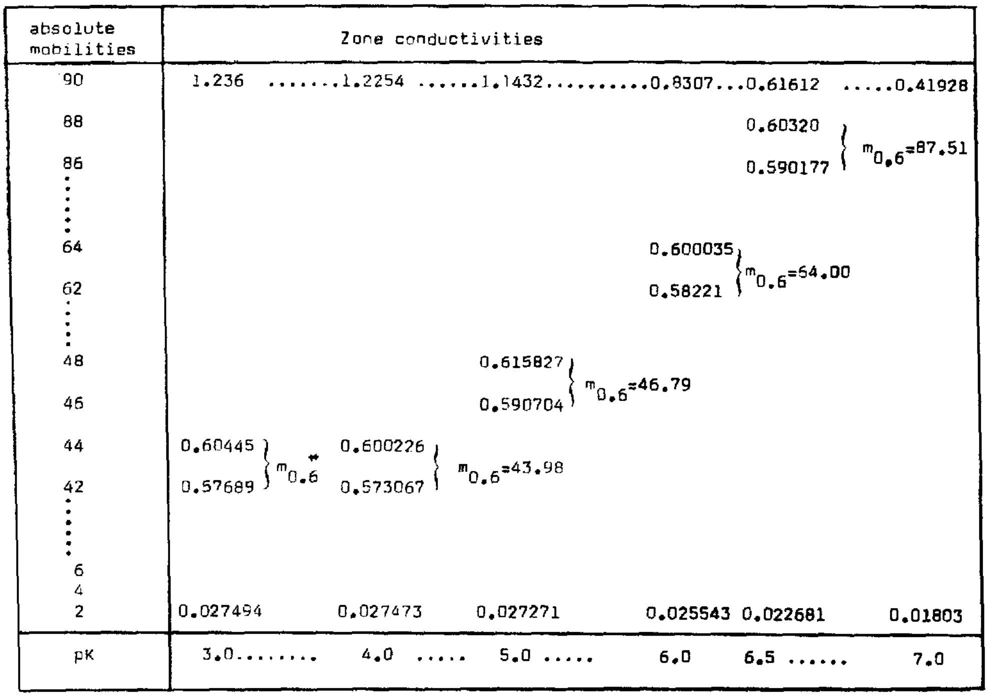
Fig. 4. Some isoconductors for systems at pH$_L$ values of 6.02 and 7.05. Note that for a certain pK value the isoconductor values for a given electrolyte show a linear relationship with the absolute mobilities (10^{-5} cm^2/Vsec) associated with them.

systems with pH_L values of 6.02 and 7.05. It can be concluded that for ionic species with p*K* values up to *ca.* 5 no information can be obtained about their p*K* values as they are nearly fully ionised. The best way to find p*K* values is to choose a pH_L interval of the two electrolyte systems such that the p*K* values are included, *i.e.* if the pH_L values are chosen to be 3 and 6 nearly all p*K* values can be found.

METHOD OF CALCULATION

In the theoretical part we have introduced the concept of isoconductors and shown how absolute mobilities and p*K* values can be obtained from the intersection of two isoconductors. In practice the calculations take a very long time, because of the great number of iterations in the computer program. The calculation of one intersection of two isoconductors takes *ca.* 2 h and that is why another method of calculation has been chosen.

If we look at the isoconductor values in a given electrolyte system, it is evident that at a certain p*K* value a nearly linear relationship exists between the absolute mobilities and isoconductor values concerned. This fact has been used for our calculations.



absolute mobilities	Zone conductivities										
90	1.236	......	1.2254	......	1.1432	....	0.8307	...	0.61612	.....	0.41928
88									0.60320	$m_{0.6}=87.51$	
86									0.590177		
⋮											
64							0.600035	$m_{0.6}=64.00$			
62							0.58221				
⋮											
48					0.615827	$m_{0.6}=46.79$					
46					0.590704						
44	0.60445	$m_{0.6}$ *	0.600226	$m_{0.6}=43.98$							
42	0.57689		0.573067								
⋮											
6											
4											
2	0.027494		0.027473		0.027271		0.025543		0.022681		0.01803
pK	3.0	....	4.0	.....	5.0	.....	6.0		6.5	......	7.0

Fig. 5. Two-dimensional array of calculated zone conductivities (pH_L = 6.02) for p*K* values from 3.0 to 7.0 and absolute mobilities from 2 to 90. Isoconductors can be obtained by interpolating between the two most adjacent zone conductivities. At a p*K* value of 3.0 the absolute mobility for an isoconductor with a value of 0.6 can be obtained as follows:

$$m_{0.6} = 42 + 2\frac{0.6 - 0.57689}{0.60445 - 0.57689} = 43.68$$

For all electrolyte systems used in the experimental part we calculated all zone conductivities for pK values from 3.0 to 7.0 (in steps of 0.1) and for absolute mobilities from 2 to 90 (in steps of 2) and collected them in a two-dimensional array (see Fig. 5).

If an isoconductor is needed for an electrolyte system we look for it in this array by interpolating between the two most adjacent zone conductivities for all pK values between 3.0 and 7.0.

If we want to determine an intersection between two isoconductors, we compute the isoconductors from the arrays and determine the intersection between these isoconductors as the intersection of two straight lines through the most adjacent mobilities to this intersection (see Fig. 6).

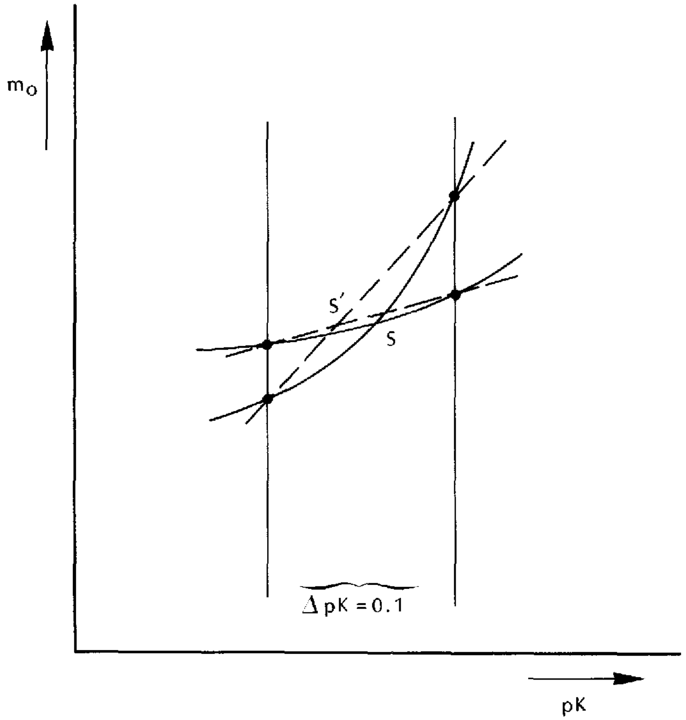


Fig. 6. S' is the estimated intersection point of two isoconductors, and S is the real point of intersection. For further explanation see text.

This procedure of calculating of an intersection takes *ca.* 1 min, which can even be shortened by a factor of *ca.* 7 using a basic compiler*.

Values of the absolute mobilities obtained in this way differ by less than 0.1% from those obtained by the computer program in Fig. 3.

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* All calculations have been carried out with a TRS-80 microcomputer.

TABLE I

THE CONDITIONS FOR THE LEADING ELECTROLYTE SYSTEMS USED

pH leading zone	*Concentration leading ionic species (mol/l)*	*Leading ion*	*Absolute mobility (10^{-5} cm²/Vsec)*	*pK*	*Counter-ionic species**	*Absolute mobility (10^{-5} cm²/Vsec)*	*pK*
3.0	0.01	Cl^-	79.08	−3	β-Ala^+	31.0	3.55
4.5	0.01	Cl^-	79.08	−3	ε-AMC	28.8	4.43
6.02	0.01	Cl^-	79.08	−3	His^+	29.6	6.04
7.05	0.01	Cl^-	79.08	−3	$Imid^+$	52.0	6.95
7.5	0.01	Cl^-	79.08	−3	$Tris^+$	29.5	8.08.

* β-Ala^+ = β-alanine; ε-AMC = ε-aminocaproic acid; His^+ = histidine; $Imid^+$ = imidazole.

EXPERIMENTAL

To test the preceding theory for its applicability and accuracy we have made use of data already published[1,2]. This has been done to try the applicability for both thermometric and potentiometric detection; in addition, the results obtained can be compared with those of Hirokawa *et al.*[3], who used the same data for the determination of absolute mobilities.

Relationship between step-heights and zone conductivities

For seven monovalent acids for which the absolute mobilities and pK values are well known, the zone conductivities* have been calculated with a computer program[1] for five electrolyte systems. The conditions of these five systems are listed in Table I.

The step-heights, mobilities and pK values, calculated zone conductivities and reciprocal conductivities for the seven monovalent acids are given in Table II.

In order to obtain information from step-heights measured with regard to zone conductivities, we set up the relationships between step-heights and reciprocal zone conductivities using data from Table II.

As an example, Fig. 7 shows the relationship between step-heights and reciprocal zone conductivities for electrolyte systems with pH_L values of 4.5, 6.02 and 7.5. For these systems identical relationships were obtained, because the absolute mobilities of the counter-ionic species are nearly equal. For example, for thermometric detection (pH_L 6.02 and 7.05) different lines were obtained. With such a relationship all step-heights can be converted into zone conductivities.

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* The numbers we posit as zone conductivities are not real conductivities, in fact, but values proportional to them. Instead of the expression $\lambda = \Sigma_i c_i m_i F$ (where F is the Faraday constant, $9.65 \cdot 10^4$), we used the expression $\lambda = \Sigma_i c_i m_i$ for calculation of the zone conductivity. We also neglected the factor 10^{-5} in the value of the absolute mobility, which is in general *ca.* $20–80 \cdot 10^{-5}$ cm²/Vsec. This is of no interest for the computations.

Of course, all conductivities calculated can be converted into real conductivities by multiplying by a constant factor.

TABLE II

STEP-HEIGHTS (H), ABSOLUTE MOBILITIES, pK VALUES, ZONE CONDUCTIVITIES (λ) AND RECIPROCAL CONDUCTIVITIES ($1/\lambda$) FOR SEVEN MONOVALENT ACIDS IN SEVERAL ELECTROLYTE SYSTEMS

The step-heights and calculated reciprocal conductivities have been used to plot the curves shown in Fig. 7.

	Absolute mobility (10^{-5} cm^2/Vsec)	*pK*		*pH*					
				*3.0**	*4.5**	*6.02**	*7.5**	*6.02***	*7.05***
Acetic acid	42.4	4.756	H (mm)	3880	1090	484	466	366	281
			λ	0.1553	0.3477	0.5600	0.5814	0.5600	0.7002
			$1/\lambda$	6.439	2.876	1.786	1.720	1.786	1.428
Caproic acid	30.4	4.90	H (mm)	6520	1930	905	859	478	386
			λ	0.1017	0.2354	0.3989	0.4167	0.3989	0.5018
			$1/\lambda$	9.833	4.248	2.507	2.400	2.507	1.993
Chloric acid	66.8	−2.7	H (mm)	100	100	100	100	243	190
			λ	1.2102	0.9202	0.9183	0.9173	0.9183	1.1073
			$1/\lambda$	0.826	1.087	1.089	1.090	1.089	0.9031
Formic acid	57.0	3.77	H (mm)	1010	285	208	209	276	216
			λ	0.4611	0.6913	0.7783	0.7812	0.7783	0.9428
			$1/\lambda$	2.169	1.447	1.285	1.280	1.285	1.061
Iodic acid	41.95	0.77	H (mm)	498	500	464	460	358	290
			λ	0.7571	0.5778	0.5767	0.5760	0.5767	0.6954
			$1/\lambda$	1.321	1.731	1.734	1.736	1.734	1.438
Perchloric acid	69.9	−2	H (mm)	69	63	75	72	–	–
			λ	1.2663	0.9629	0.9609	0.9598		
			$1/\lambda$	0.790	1.039	1.041	1.0142		
Phenylacetic acid	31.5	4.33	H (mm)	3680	1210	823	814	448	366
			λ	0.1776	0.3296	0.4270	0.4323	0.4270	0.5215
			$1/\lambda$	5.631	3.034	2.342	2.313	2.342	1.918
Leading zone HCl	79.08	−3	H (mm)	0	0	0	0	–	–
			λ	1.4326	1.0894	1.0871	1.0856		
			$1/\lambda$	0.698	0.918	0.920	0.921		

* Potentiometric detection.
** Thermometric detection.

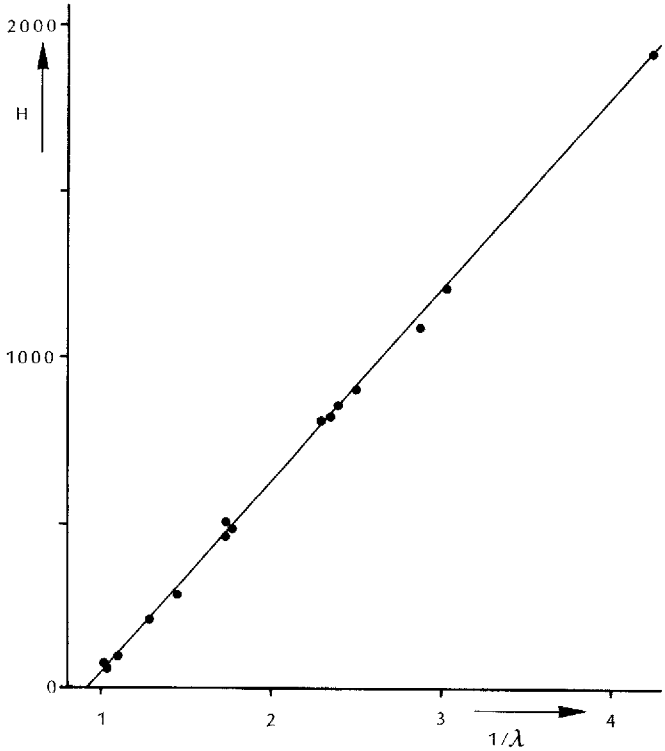

Fig. 7. An example of the relationship between measured step-heights (in millimetres) and reciprocal conductivities for systems at pH_L values of 4.5, 6.02 and 7.5.

The calculation of absolute mobilities from pK values and zone conductivities

The absolute mobilities of ionic species can be calculated from step-heights (zone conductivities) and p*K* values. In fact, the intersection of the isoconductor concerned and a p*K* value (see Fig. 1) is determined. This is done for some monovalent acids for which the step-heights have already been reported [1,2].

With a relationship as shown in Fig. 7, for example for potentiometric detection for pH_L values of 4.5, 6.02 and 7.5, step-heights are converted into zone conductivities and, with a computer program, the absolute mobilities are calculated from the zone conductivities and known p*K* values. We used the p*K* values given by Hirokawa *et al.*[3], because he used the same step-heights for the computations of mobilities with the concept of the R_E values. So we can compare the results.

Calculations have been made for step-heights measured both by thermometric and by potentiometric detection. Table III lists all the calculated absolute mobilities. Furthermore, the average absolute mobilities are given as well as the values obtained by Hirokawa. In general, there is a great similarity with the values of Hirokawa, although we did not correct for the influence of activity coefficients, complex formation, etc.

For some ionic species different values have been obtained for the different systems, caused by measuring faults (not all step-heights have been measured with the same apparatus and detector!), inexact p*K* values, and other factors.

For the calculation of pK values and absolute mobilities from the intersection of two isoconductors, we used those step-heights giving a nearly equal value of the absolute mobility for two electrolyte systems in Table III.

TABLE III

ABSOLUTE MOBILITIES (10^{-5} cm^2/Vsec) CALCULATED FROM ZONE CONDUCTIVITIES AND pK VALUES FOR SEVERAL ELECTROLYTE SYSTEMS

	pH$_L$						*Average*	*Hirokawa*[3]
	*3.0**	*4.5**	*6.02**	*7.5**	*6.02***	*7.05***		
Acetic acid	44.80	43.41	43.04	42.03	41.70	42.65	42.94	42.4
Acetic acid phenyl	30.70	31.93	31.41	31.21	32.11	31.79	31.53	31.5
Benzoic acid	33.62	29.70	33.64	33.51	33.55	36.38	33.40	32.9
Benzoic acid, *p*-amino	33.20	33.39	32.28	32.29	32.87	33.49	32.92	32.3
Benzoic acid, 2,4-dihydroxy	29.89	29.59	31.46	33.10	30.79	32.80	31.27	31.8
Benzoic acid, *p*-nitro	30.19	30.86	32.24	32.52	32.16	33.90	31.98	32.1
Butyric acid	34.41	40.69	34.07	30.91	34.78	32.91	34.63	33.7
Caproic acid	30.88	30.61	30.62	30.21	30.86	30.15	30.56	30.5
Caprylic acid	27.92	26.07	27.57	27.22	28.61	27.88	27.55	27.4
Chloric acid	65.72	66.58	66.73	66.81	66.75	67.03	66.60	66.6
Enanthic acid	28.89	28.58	28.89	28.38	–	–	28.69	28.7
Formic acid	60.34	58.92	57.13	56.91	56.92	57.49	57.95	57.1
Glucoronic acid	24.39	24.04	26.85	27.03	27.40	27.31	26.17	26.6
Glycerinic acid	35.43	35.41	36.22	36.74	–	–	35.95	36.3
Glycolic acid	42.71	42.89	42.76	41.98	41.09	41.77	42.20	42.3
Iodic acid	40.15	40.56	42.17	42.34	–	41.04	41.25	41.9
Lactic acid	36.59	29.56	37.10	37.34	37.24	37.61	35.91	35.8
Laevulinic acid	34.41	32.51	33.71	33.59	34.01	–	33.65	33.4
Methacrylic acid	37.66	36.08	37.22	36.36	36.37	37.89	36.93	36.6
Pivalic acid	31.49	33.16	32.01	31.05	–	–	31.93	31.6
Propionic acid	39.70	35.13	37.40	37.02	–	–	37.31	36.9
Propionic acid, *β*-chloro	36.82	34.77	36.27	38.33	36.36	37.35	36.65	36.8

* Potentiometric detection.
** Thermometric detection.

The calculation of pK values and absolute mobilities from the intersection of two isoconductors

In order to establish whether the above method for the determination of absolute mobilities and pK values of ionic species from the intersection of two isoconductors can be used in practice, some computations have been carried out with a computer program.

Table IV shows the results for the calculations using the step-heights of electrolyte systems at pH$_L$ values of 4.5 and 6.02. The results are divided into three groups: (A) the cases in which the absolute mobilities in Table III are nearly equal; (B) the cases in which the absolute mobilities differ by *ca.* 1–2; and (C) the cases with larger differences in absolute mobilities.

For groups A and B (for which the absolute mobilities as obtained in Table

TABLE IV

ABSOLUTE MOBILITIES (10^{-5} cm^2/Vsec) AND p*K* VALUES CALCULATED FROM THE INTERSECTION OF TWO ISOCONDUCTORS FOR SEVERAL ELECTROLYTE SYSTEMS

	Zone conductivity		*Calculated*		*Hirokawa*[3]	
	pH_L 4.5	*pH_L 6.02*	*pK*	*Mobility*	*pK*	*Mobility*
A Acetic acid	0.3546	0.5682	4.745	43.0	4.756	42.4
Acetic acid, phenyl	0.3306	0.4255	4.31	31.35	4.351	31.5
Caproic acid	0.2347	0.4008	4.915	30.6	4.913	30.5
Enanthic acid	0.2268	0.3795	4.89	28.9	4.887	28.7
Glycerinic acid	0.4464	0.4963	3.77	36.3	3.656	36.3
Glycolic acid	0.5155	0.5848	3.845	42.76	3.85	42.3
B Benzoic acid, *p*-nitro	0.4049	0.4425	3.61	32.3	3.391	32.1
Caprylic acid	0.2016	0.3610	5.015	27.85	4.93	27.4
Formic acid	0.7092	0.7813	3.65	57.05	3.796	57.1
Methacrylic acid	0.3527	0.5013	4.52	37.35	4.458	36.6
Pivalic acid	0.2364	0.4141	4.95	31.8	5.007	31.6
Propionic acid, *β*-chloro	0.4264	0.4963	3.97	36.36	3.804	36.8
C Benzoic acid	0.3322	0.4577	4.465	33.9	4.166	32.9
Butyric acid	0.3247	0.4494	4.42	33.25	4.807	33.7
Glucoronic acid	0.3115	0.3677	4.085	29.65	3.516	26.6
Lactic acid	0.3610	0.5076	4.49	37.7	3.854	35.8
Propionic acid	0.2890	0.4938	4.87	32.5	4.779	36.9

TABLE V

ABSOLUTE MOBILITIES (10^{-5} cm^2/Vsec) AND p*K* VALUES CALCULATED FROM THE INTERSECTION OF TWO ISOCONDUCTORS FOR SEVERAL ELECTROLYTE SYSTEMS

	Zone conductivity		*Calculated*		*Hirokawa*[3]	
	pH_L 3.0	*pH_L 6.02*	*pK*	*Mobility*	*pK*	*Mobility*
A Acetic acid, phenyl	0.1706	0.4255	4.367	31.30	4.351	31.5
Caproic acid	0.1018	0.4008	4.898	30.44	4.91	30.5
Caprylic acid	0.0921	0.3610	4.914	27.40	4.93	27.4
Enanthic acid	0.0987	0.3795	4.883	28.80	4.887	28.7
Glycolic acid	0.3378	0.5848	3.852	42.76	3.85	42.3
B Benzoic acid	0.2155	0.4577	4.164	33.60	4.166	32.9
Butyric acid	0.1236	0.4494	4.79	34.00	4.807	33.7
Glucoronic acid	0.2466	0.3683	3.74	26.89	3.516	26.6
Lactic acid	0.2950	0.5076	3.867	37.05	3.854	35.8
Propionic acid	0.1435	0.4938	4.717	37.20	4.779	36.9

III do not differ much, *i.e.* the experimental values in refs. 1 and 2 will be very close) a great similarity with the results of Hirokawa is observed. It is remarkable that, even for p*K* values of *ca.* 3.8 (glycolic and glycerinic acid), the results show a good agreement. For ionic species with differences in absolute mobilities in the different systems in Table III (group C) the results do not agree.

Table V shows the results for the calculations of p*K* values and absolute mobilities for electrolyte systems at pH_L values of 3.0 and 6.02. This pH_L interval covers nearly all p*K* values. The results in part A are for some ionic species with nearly equal mobilities in Table III. In part B the results are for the ionic species in group C of Table IV. As we can see the agreement for the latter group is now much better, which is to be expected because the absolute mobilities for these electrolyte systems (pH_L 3.0 and 6.02) show a better similarity in Table III.

Table VI shows some calculations for ionic species with p*K* values of *ca.* 3.5 using step-heights of the electrolyte systems at pH_L values of 3.0 and 4.5. The p*K* values obtained correspond with those obtained by Hirokawa; the question, however, is which mobilities are better as they differ from those obtained for other electrolyte systems.

TABLE VI

ABSOLUTE MOBILITIES (10^{-5} cm^2/Vsec) AND p*K* VALUES CALCULATED FROM THE INTERSECTION OF TWO ISOCONDUCTORS FOR SEVERAL ELECTROLYTE SYSTEMS

	Zone conductivity		*Calculated*		*Hirokawa*[3]	
	pH_L 3.0	*pH_L 4.5*	*pK*	*Mobility*	*pK*	*Mobility*
Formic acid	0.4739	0.7092	3.765	58.55	3.796	57.1
Benzoic acid, *p*-nitro	0.3413	0.4049	3.415	31.0	3.391	32.1
Glucoronic acid	0.2639	0.3115	3.495	23.9	3.516	26.6
Glycolic acid	0.3378	0.5155	3.86	42.9	3.85	42.3
Propionic acid, *β*-chloro	0.3077	0.4264	3.715	34.2	3.804	36.8

CONCLUSIONS

From the preceding calculations it can be concluded that p*K* values and absolute mobilities can be obtained from the intersections of two isoconductors. The results obtained correspond with values available in the literature and those computed by Hirokawa *et al.* with his concept of R_E values, provided that the zone conductivities (step-heights) are exactly known. For the calculations it is sufficient to measure the step-heights in two electrolyte systems at pH_L values of 3.0 and 6.02, because this pH interval covers nearly all p*K* values.

Corrections, *e.g.* for activity coefficients and complex formation, seem unnecessary for monovalent ionic species, particularly if step-heights are measured for electrolyte systems at low concentrations.

In principle, analogue computations can be carried out for cationic species and even for divalent ionic species, if their p*K* values differ sufficiently.

REFERENCES

1 F. M. Everaerts, J. L. Beckers and Th. P. E. M. Verheggen, *Isotachophoresis, Theory, Instrumentation and Applications*, Elsevier, Amsterdam, 1976.
2 J. L. Beckers, *Thesis*, University of Technology, Eindhoven, 1973.
3 T. Hirokawa, M. Nishino and Y. Kiso, *J. Chromatogr.*, 252 (1982) 49.