

Extrapolation of Kinetic Data for Reactions Involving Weak Electrolytes

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To enable direct comparison of rate constants for bimolecular reactions in which one of the reactants is a weak electrolyte, extrapolation to infinite dilution has to be performed. One method of accomplishing this extrapolation is to apply the Acree equation to the kinetic data. This procedure requires a predetermined association constant of the ionizable reactant, *e.g.* from electrical conductance data. In this article a method of extrapolation, requiring no independently determined association constant, is outlined. Rate constants extrapolated by this method for 23 different systems involving alkali halides and two systems involving tetraalkyl ammonium halides are compared with the corresponding rate constants derived from the Acree equation. The values extrapolated by means of the two different methods agree very well, the relative deviations being usually less than 2 %.

In analyzing kinetic data for second-order displacement reactions of the type



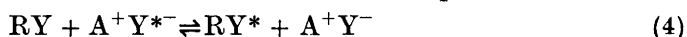
where RY denotes a nonionizable reactant and AY is a weak electrolyte, we may employ the Acree equation

$$k = k_i \alpha + k_m (1 - \alpha) \quad (2)$$

in which k is the overall rate constant, k_i the rate constant for the reaction between RY and free ions



k_m the rate constant for the reaction between RY and ion-pairs



and α the degree of dissociation of the ionic reactant.

Several examples of the analysis of kinetic data by this means for displacement reactions involving organic halides and alkali halides may be found in the literature, *e.g.* Refs. 1-3.

According to eqn. (2) the association constant, K_A , of the ionizable reactant is required for calculation of α .

The purpose of the present paper is to describe a method, which permits evaluation of k_i without *a priori* knowledge of the association constant and to compare the values of k_i obtained by this means with values calculated from eqn. (2) using values of α derived from electrical conductance data.

DERIVATION

For several reactions of type (1) it has been found that the rate constant for reaction (4) involving RY and paired ions is much less than the rate constant for reaction (3) involving RY and free ions, *i.e.* $k_m \ll k_i$; see for instance Ref. 1. In fact, several reactions may be quoted in which k_m has been found to be zero within experimental errors. In such cases, and/or if the reaction is studied at sufficient dilution for α to be close to unity, we may neglect the second term on the right-hand side of eqn. (2) *i.e.*

$$k = k_i \alpha \quad (5)$$

If the ionic reactant forms ion-pairs, but no higher aggregates, we have to consider the equilibrium



Application of the law of mass action to this equilibrium yields

$$K_A = \frac{1 - \alpha}{c\gamma^2\alpha^2} \quad (7)$$

where c is the analytical concentration of the ionic reactant and γ the mean molar activity coefficient.

Eliminating α between eqns. (5) and (7) yields the following equation:

$$\frac{1}{k} = \frac{1}{k_i} + \frac{K_A c \gamma^2 k}{k_i^2} \quad (8)$$

according to which k_i may be obtained from the intercept of the straight line which should result upon plotting $1/k$ vs. $c\gamma^2 k$; *cf.* Ref. 4.

From eqns. (5) and (8) it may be seen that the method of calculation outlined implicitly involves the use of an ion-pair association constant based on the kinetic data.

RESULTS AND DISCUSSION

In comparing extrapolated rate constants, k_i , according to the two different expressions, eqns. (2) and (8), we shall restrict ourselves to kinetic data⁴⁻¹⁰ for isotopic exchange reactions between organic and inorganic halides obtained at this institute during the last few years.

A compilation of these reactions with pertinent references to the papers containing primary kinetic data is shown in Table 1. These reactions, which all appear to be of S_N2 -type, were investigated by means of ¹³¹I, ⁸²Br, or ³⁶Cl

Table 1. Compilation of reactions analyzed by means of eqns. (2) and (8).

Reactants	Solvent	Ref.
CH ₃ I + NaI, KI, RbI, or CsI	Methanol	5
CH ₃ I + NaI, KI, RbI, or CsI	Ethanol, 6.3 wt. % aq.	6
CH ₃ I + NaI, KI, RbI, or CsI	Ethanol	7
CH ₃ I + NaI, KI, RbI, or CsI	Propanol	8
C ₄ H ₉ Br + LiBr	Acetone, 1.5 wt. % aq.	9
C ₄ H ₉ Br + LiBr	Acetone, 1.0 wt. % aq.	9
C ₄ H ₉ Br + LiBr	Acetone, 0.6 wt. % aq.	9
C ₄ H ₉ Br + LiBr	Acetone, 0.3 wt. % aq.	9
C ₄ H ₉ Br + LiBr	Acetone, 0.1 wt. % aq.	9
C ₄ H ₉ Br + LiBr	Acetone	9
<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Cl + LiCl	Acetone	4
C ₄ H ₉ Br + (C ₄ H ₉) ₄ NBr	Acetone	10
<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Cl + (C ₄ H ₉) ₄ NCl	Acetone	10

as radioactive indicators. The primary kinetic data consist of overall second-order rate constants, k , according to the McKay equation for several concentrations below 0.01 M of the ionic reactant.

Mean molar activity coefficients were estimated by means of the Debye-Hückel equation in the form given in Ref. 4 using the permittivities of pure solvents and solvent mixtures listed in Table 2. Because of the dilute solutions used the difference between molar and rational activity coefficients was ignored.

In calculating k_i from eqn. (2) the association constants and ion-size parameters listed in Table 3 were used. The method employed to calculate k_i has been described.⁴ With one exception (lithium chloride in acetone) the values of K_A and \bar{a} in Table 3 were derived from electrical conductance data by means of the Fuoss-Onsager equation¹⁵ of 1957. The association constant for lithium chloride in pure acetone was obtained from the dissociation constant, $K_D = 2.8 \times 10^{-6}$ M, reported in a recent paper by Brookes *et al.*¹⁴ who

Table 2. Permittivities of anhydrous and aqueous solvents at 25.0°C.

Solvent	ϵ	Ref.
Methanol	32.6	11
Ethanol, 6.3 wt. % aq.	27.1	6
Ethanol	24.3	11
Propanol	20.4	8
Acetone, 1.5 wt. % aq.	21.3	12
Acetone, 1.0 wt. % aq.	21.2	13
Acetone, 0.6 wt. % aq.	20.9	13
Acetone, 0.3 wt. % aq.	20.8	13
Acetone, 0.1 wt. % aq.	20.8	13
Acetone	20.7	13

Table 3. Ion-pair association constants and ion-size parameters at 25.0°C.

Solvent	Salt	K_A M ⁻¹	$\bar{a} \times 10^8$ cm	Ref.
Methanol	NaI	2.2	4.3	11
Methanol	KI	2.3	4.0	11
Methanol	RbI	6.0	4.0	11
Methanol	CsI	9.4	3.8	11
Ethanol, 6.3 wt. % aq.	NaI	13.2	4.7	6
Ethanol, 6.3 wt. % aq.	KI	18.9	4.0	6
Ethanol, 6.3 wt. % aq.	RbI	34.4	4.4	6
Ethanol, 6.3 wt. % aq.	CsI	52.2	4.3	6
Ethanol	NaI	8.5	3.9	11
Ethanol	KI	39.1	4.2	11
Ethanol	RbI	63.6	4.2	11
Ethanol	CsI	98.9	4.2	11
Propanol	NaI	112	4.7	8
Propanol	KI	279	5.3	8
Propanol	RbI	431	6.8	8
Propanol	CsI	622	8.0	8
Acetone, 1.5 wt. % aq.	LiBr	1 640	3.9	12
Acetone, 1.0 wt. % aq.	LiBr	2 073	5.4	13
Acetone, 0.6 wt. % aq.	LiBr	2 383	5.2	13
Acetone, 0.3 wt. % aq.	LiBr	2 786	6.4	13
Acetone, 0.1 wt. % aq.	LiBr	3 360	6.6	13
Acetone	LiBr	4 202	9.3	13
Acetone	LiCl	357 000	2.4 ^a	14
Acetone	(C ₄ H ₉) ₄ NBr	349	7.2	10
Acetone	(C ₄ H ₉) ₄ NCl	481	6.3	10

^a Crystal radii sum.

evaluated K_D from conductance data according to the method of Fuoss.¹⁶ An attempt to fit the Fuoss-Onsager equation¹⁵ to the latter data by means of a computer programme in Ref. 11 was unsuccessful.

Extrapolation of kinetic data to infinite dilution by means of eqn. (8) was performed by fitting this equation to experimental data by means of the

Table 4. Dependence of k_i according to eqn. (8) on the ion-size parameter, \bar{a} .

Reactants	Solvent	$\bar{a} \times 10^8$ cm	$k_i \times 10^8$ M ⁻¹ s ⁻¹
CH ₃ I + CsI	Propanol	4.0	13.99
		8.0 ^a	13.98
C ₄ H ₉ Br + LiBr	Acetone	4.0	7.857
		9.3 ^a	7.588
<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Cl + LiCl	Acetone	4.0	43.24
		2.4 ^a	43.41

^a Value derived from electrical conductance data using the Fuoss-Onsager equation.¹⁵

Table 5. Comparison of k_i according to eqns. (2) and (8) for the exchange of iodine between methyl iodide and alkali iodides in different solvents at 25.0°C.

Solvent	$k_i \times 10^3$ $M^{-1} s^{-1}$ Eqn. (2)	$k_i \times 10^3$ $M^{-1} s^{-1}$ Eqn. (8)	$\frac{k_i, \text{eqn. (8)}}{k_i, \text{eqn. (2)}}$
		NaI	
Methanol	3.320	3.320	1.000
Ethanol, 6.3 wt. % aq.	10.72	10.73	1.001
Ethanol	10.39	10.40	1.001
Propanol	13.68	13.71	1.002
		KI	
Methanol	3.332	3.335	1.001
Ethanol, 6.3 wt. % aq.	10.70	10.71	1.001
Ethanol	10.36	10.36	1.000
Propanol	13.98	13.93	0.996
		RbI	
Methanol	3.309	3.309	1.000
Ethanol, 6.3 wt. % aq.	10.69	10.70	1.001
Ethanol	10.36	10.36	1.000
Propanol	13.92	13.76	0.989
		CsI	
Methanol	3.301	3.301	1.000
Ethanol, 6.3 wt. % aq.	10.75	10.75	1.000
Ethanol	10.42	10.42	1.000
Propanol	13.99	13.99	1.000

relative deviation least squares method since the relative error in $1/k$ appears to be independent of $c\gamma^2k$ for the range of concentrations investigated; cf. Ref. 4. Activity coefficients, γ , were calculated as reported above with the exception that the value, $\hat{a} = 4 \text{ \AA}$, for the ion-size parameter was used throughout. The exact choice of \hat{a} -value in evaluating k_i from eqn. (8) appears not to be very critical as may be seen from the data in Table 4.

The results of these calculations are shown in Tables 5–7 in which values of k_i according to eqns. (2) and (8) have been listed in the second and third columns, respectively.

Table 6. Comparison of k_i according to eqns. (2) and (8) for the exchange of bromine between butyl bromide and lithium bromide in aqueous acetone at 25.0°C.

Wt. % water in solvent mixture	$k_i \times 10^3$ $M^{-1} s^{-1}$ Eqn. (2)	$k_i \times 10^3$ $M^{-1} s^{-1}$ Eqn. (8)	$\frac{k_i, \text{eqn. (8)}}{k_i, \text{eqn. (2)}}$
1.5	1.656	1.697	1.025
1.0	2.533	2.602	1.027
0.6	3.370	3.337	0.990
0.3	4.067	4.046	0.995
0.1	6.805	7.003	1.029

Table 7. Comparison of k_i according to eqns. (2) and (8) for halogen exchange reactions in "dry" acetone at 25.0°C.

Reactants	$k_i \times 10^3$ $M^{-1} s^{-1}$ Eqn. (2)	$k_i \times 10^3$ $M^{-1} s^{-1}$ Eqn. (8)	$\frac{k_i, \text{eqn. (8)}}{k_i, \text{eqn. (2)}}$
$C_6H_5Br + LiBr$	7.850	7.857	1.001
$p\text{-NO}_2C_6H_4CH_2Cl + LiCl$	43.68	43.24	0.990
$C_6H_5Br + (C_4H_9)_4NBr$	7.067	6.997	0.990
$p\text{-NO}_2C_6H_4CH_2Cl + (C_4H_9)_4NCl$	34.25	34.12	0.996

For alkali iodides in methanol and in anhydrous and aqueous ethanol, where these salts are only slightly associated under the conditions used, there is excellent agreement between the values of k_i according to the two different methods of calculation, the discrepancies being 0.1 % or less; see the last column in Table 5.

For the other systems investigated, where association to ion-pairs is more extensive, which implies longer extrapolations, the agreement between the two methods of calculation is very satisfactory. For these systems the values of k_i according to eqns. (2) and (8) deviate by only 1 or 2 %, see Tables 5–7.

The *p*-nitrobenzyl chloride-lithium chloride exchange reaction in acetone⁴ represents an extreme example of a system for which the determination of the rate constant at infinite dilution involves a very long extrapolation. This may be seen in Fig. 1 in which the overall second-order rate constant has been

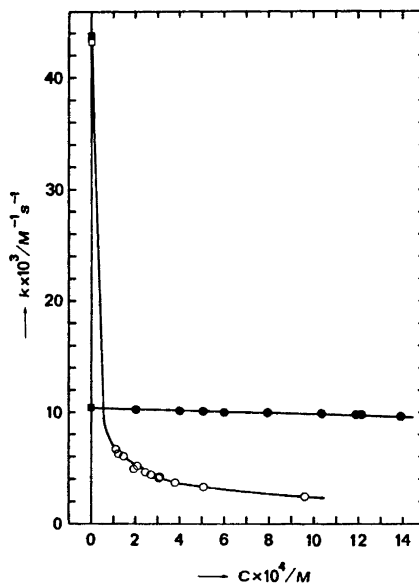


Fig. 1. Dependence of the overall second-order rate constant at 25.0°C on the analytical concentration of the ionic reactant for exchange of ^{36}Cl between *p*-nitrobenzyl chloride and lithium chloride in acetone (open circles) and for exchange of ^{131}I between methyl iodide and cesium iodide in ethanol (full circles) according to Refs. 4 and 7, respectively. The points denoted by squares at zero concentration were calculated from eqns. (2) and (8). Full squares, eqn. (2). Open square, eqn. (8). (The points at $c=0$ according to these two equations coincide for the iodine exchange reaction.)

plotted (open circles) against the analytical concentration of lithium chloride. Under the experimental conditions⁴ the concentration of lithium chloride ion-pairs greatly exceeds the concentration of unpaired chloride ions ($0.06 < \alpha < 0.17$). Nevertheless, the rate constants extrapolated to zero concentration by means of eqns. (2) and (8) agree within 1 %.

In comparison, a much shorter extrapolation is needed when association to ion-pairs is relatively unimportant as demonstrated by the rate constant *vs.* concentration curve in Fig. 1 (full circles) for the methyl iodide-cesium iodide exchange reaction in ethanol.⁷ For this system the concentration of free ions is in great excess over the concentration of paired ions ($0.92 < \alpha < 0.99$). The points calculated at zero concentration by means of eqns. (2) and (8) coincide.

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