

A Modified Acree Equation for Application to Reactions Subject to Kinetic Salt Effect

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The Acree equation has been modified to take in account kinetic salt effect. The use of the extended equation is demonstrated by application to kinetic data for exchange of ^{131}I between alkali iodides (NaI, KI, RbI, and CsI) and methyl iodide in aqueous ethanol at 25°C. Comparison of rate constants evaluated from the original and modified Acree equations reveals that neglect of the salt effect, which is negative in the reactions studied, is of little importance with respect to the reactivity of free ions but results in an underestimate of the reactivity of paired ions.

Numerous investigators have observed that the specific reaction rate of certain reactions in which one reactant is a neutral molecule and the other is a weak electrolyte varies with the concentration of the latter. In accord with the Acree hypothesis¹ this effect is generally attributed to changes in ionic association and different reactivities of free ions and ion-pairs. There is, however, strong evidence that part of the concentration dependence of the specific reaction rate, contrary to the prediction of the Brønsted-Bjerrum theory² for reactions involving one uncharged reactant, is due to kinetic salt effect.³

The purpose of this paper is to discuss an Acree equation modified to take in account kinetic salt effect. The extended equation is employed to analyze kinetic data for the isotopic exchange between alkali iodides and methyl iodide in ethanol containing 6.26 % water by weight.

THE MODIFIED ACREE EQUATION

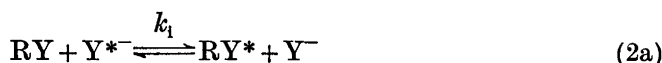
Consider a second-order isotopic exchange reaction between a nonionizable, uncharged reactant, RY, and a weak electrolyte, AY. This reaction may be represented by the gross formula

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where k is the overall second-order rate constant.

If the exchange proceeds *via* free ions, Y^- , as well as ion-pairs, which we shall denote A^+Y^- , we are concerned with the following two reactions



and



with rate constants k_i and k_m .

For reaction (2b), which in contrast to reaction (2a) involves species without net charge, we shall assume that any kinetic salt effect may be neglected.

In terms of the transition-state theory,² the rate constant for reaction (2a) may be expressed

$$k_i = \kappa \frac{kT}{h} K_0^\ddagger \frac{f_{\text{RY}} f_{\text{Y}^-}}{f^\ddagger} \quad (3)$$

where the f 's are activity coefficients and the other symbols have their usual meanings. Denoting the rate constant at infinite dilution by k_i^∞ , when activity coefficients are equal to unity, we have

$$k_i^\infty = \kappa \frac{kT}{h} K_0^\ddagger \quad (4)$$

and hence,

$$k_i = k_i^\infty f \quad (5)$$

where

$$f = \frac{f_{\text{RY}} f_{\text{Y}^-}}{f^\ddagger} \quad (6)$$

The original Acree equation¹

$$k = k_i \alpha + k_m (1 - \alpha) \quad (7)$$

in which α is the degree of dissociation of the ionizable reactant may then be written in the form

$$k = k_i^\infty \alpha f + k_m (1 - \alpha) \quad (8)$$

EXPERIMENTAL

Reagents. Sodium, potassium, rubidium, and cesium iodide were dried and labelled with ¹³¹I according to Ref. 3 in which the purification of methyl iodide is also described.

Ethanol was purified according to Ref. 4. The electrolytic conductivity of the purified solvent was $\kappa = 2 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$.

Water was distilled in a quartz apparatus and flushed with nitrogen; $\kappa = 4 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$.

Aqueous ethanol containing 6.264 % water by weight was prepared. The density of the solvent mixture, corrected for the buoyancy effect, was $d_4^{25} = 0.80349 \text{ g ml}^{-1}$, the viscosity determined using an Ubbelohde viscometer at 25°C, was $\eta = 0.01329 \text{ P}$ ($1 \text{ P} = 10^{-1} \text{ kg m}^{-1} \text{ s}^{-1}$) and the permittivity, measured by means of a Ferisol M 803 A Q-meter, was $\epsilon = 27.1$. The electrolytic conductivity varied between 2.3×10^{-8} and $5.1 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$.

Solutions were prepared by the weight dilution method and the weights corrected to vacuum.

Kinetic measurements. The rates of the isotopic exchange between methyl iodide and sodium, potassium, rubidium, and cesium radioiodide, respectively, at $25.00 \pm 0.02^\circ\text{C}$ were measured as previously described.³ The results are quoted in Table 1 in which b is the concentration of methyl iodide, c is the concentration of alkali iodide, and k is the second-order rate constant equal to R/bc where R is the rate of exchange according to the well-known McKay equation.

Table 1. Second-order rate constants for exchange of ^{131}I between methyl iodide and alkali iodides in ethanol containing 6.26 % water by weight at 25°C.

$b \times 10^2$ M	$c \times 10^4$ M	$k \times 10^3$ $\text{M}^{-1} \text{ s}^{-1}$	$b \times 10^2$ M	$c \times 10^4$ M	$k \times 10^3$ $\text{M}^{-1} \text{ s}^{-1}$
Sodium iodide			Potassium iodide		
4.049	79.2	10.14	4.071	79.3	9.67
4.005	39.84	10.37	4.067	39.69	9.96
3.994	19.92	10.51	4.080	19.82	10.24
4.012	9.90	10.52	4.031	9.89	10.47
3.997	4.950	10.67	4.063	4.986	10.55
3.980	1.983	10.73	4.097	1.995	10.69
Rubidium iodide			Cesium iodide		
4.067	78.8	9.49	4.035	39.64	9.87
4.051	39.56	9.90	4.031	19.95	10.19
4.041	19.79	10.23	4.039	9.96	10.37
4.085	9.84	10.36	4.049	4.975	10.55
4.046	4.951	10.50	4.065	1.991	10.71
4.111	1.983	10.68			

Conductivity measurements. Measurements of electrolytic conductivity at $25.00 \pm 0.01^\circ\text{C}$ were performed as described in Ref. 5 by means of a Leeds and Northrup 4666 conductivity bridge. Corrections for the electrolytic conductivity of the solvent mixture were applied. Molar conductivities, Λ , for the different salts studied are quoted in Table 2.

To obtain the ion-pair association constant, K_A , the molar conductivity at infinite dilution, Λ_∞ , and the ion-size parameter, \hat{a} , the conductivity data were fitted to the Fuoss-Onsager equation⁶ of 1957 using a computer programme outlined in Ref. 7. The values of η and ϵ quoted above for the ethanol-water solvent mixture were used in the calculations. The results are summarized in Table 3 in which the standard deviation in the single Λ -value is given in the last column. Errors attached to K_A and Λ_∞ are standard deviations.

DISCUSSION

Kinetic data from the original Acree equation. Values of k_i and k_m according to the original Acree equation, eqn. (7), were obtained by fitting a straight line to values of k/α vs. $(1-\alpha)/\alpha$ by the method of least squares. The rate

Table 2. Conductance data for salts in ethanol containing 6.26 % water by weight at 25°C.

$c \times 10^4$ M	Run A Λ $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$c \times 10^4$ M	Run B Λ $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
Sodium iodide			
34.839	39.056	38.733	38.733
28.059	39.744	32.687	39.298
27.999	39.758	24.929	40.102
19.824	40.717	13.125	41.802
11.838	42.050	6.236	43.299
5.423	43.579	5.959	43.399
3.9436	44.078	2.2743	44.807
1.9150	44.913		
Potassium iodide			
41.962	40.194	35.087	40.921
36.974	40.704	27.168	41.865
31.561	41.298	21.725	42.630
20.648	42.807	20.135	42.886
14.944	43.864	14.173	43.994
7.026	45.736	5.806	46.129
5.376	46.306	4.4713	46.654
2.2680	47.582	1.8389	47.797
Rubidium iodide			
40.377	40.233	38.502	40.459
31.946	41.266	33.800	41.036
31.544	41.319	30.808	41.421
20.514	42.998	23.817	42.440
14.044	44.350	13.731	44.392
6.832	46.325	6.846	46.315
4.8095	47.091	4.7790	47.097
2.3769	48.260	2.2310	48.318
Cesium iodide			
36.191	40.060	41.587	39.439
32.225	40.705	28.333	41.322
21.569	42.536	20.348	42.764
11.451	44.986	10.943	45.132
5.220	47.202	4.9369	47.400
3.7929	47.890	3.6335	47.983
		1.9229	49.011

Table 3. Conductance parameters for salts in ethanol containing 6.26 % water by weight at 25°C.

Salt	K_A M^{-1}	Λ_∞ $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$\lambda \times 10^8$ cm	$\sigma(\Lambda)$ %
NaI	13.2 ± 0.5	46.81 ± 0.007	4.7	0.07
KI	18.9 ± 0.3	49.79 ± 0.005	4.0	0.05
RbI	34.4 ± 0.2	50.65 ± 0.004	4.4	0.04
CsI	52.2 ± 0.3	51.31 ± 0.009	4.3	0.07

Table 4. Rate constants, k_i and k_m , for reactions of unpaired and paired iodide ions according to the original Acree equation.

Salt	$k_i \times 10^3$ $M^{-1} s^{-1}$	$k_m \times 10^3$ $M^{-1} s^{-1}$
NaI	10.72 ± 0.03	-3.1 ± 1.3
KI	10.70 ± 0.03	-7.9 ± 1.0
RbI	10.69 ± 0.03	-1.6 ± 0.5
CsI	10.75 ± 0.03	1.1 ± 0.5

constants obtained by this means, together with their standard deviations, are quoted in Table 4. According to the data in the last column, values of k_m for the exchange reactions involving sodium, potassium, and rubidium iodide are negative. This may be explained by the presence of a negative kinetic salt effect, neglect of which results in underestimation of k_m (cf. Ref. 3).

Correction for kinetic salt effect. To evaluate k_i^∞ and k_m from the extended Acree equation, eqn. (8), the dependence of the activity coefficient fraction, $f = f_{R^+} f_{Y^-} / f^\ddagger$, on the ionic strength, $\mu = c\alpha$, is required. This dependence was obtained as follows from the kinetic data for the exchange reaction involving the least associated of the salts studied, viz. sodium iodide.

According to eqn. (8) the factor, f , is given by the expression

$$f = \frac{k - k_m(1 - \alpha)}{k_i^\infty \alpha} \quad (9)$$

Hence, to evaluate f , values of k_m and k_i^∞ are needed (besides k and α).

From the data in Tables 1 and 3 we find that, for a given ionic strength, the overall rate constant, k , decreases with increasing ion-pair association constant, K_A . As discussed in a previous paper³ this behaviour implies that the reactivity of paired ions is less than the reactivity of free ions. Hence, k_m is restricted to the interval

$$0 \leq k_m < k_i^\infty \quad (10)$$

Denoting by f_1 and f_2 the factor f for the two extreme values corresponding to $k_m = 0$ and $k_m = k_i^\infty$, we have according to eqn. (9)

$$f_1 = \frac{k}{k_i^\infty \alpha} \quad (11)$$

and

$$f_2 = \frac{k - k_i^\infty(1 - \alpha)}{k_i^\infty \alpha} \quad (12)$$

respectively.

The dependence of f_1 and f_2 according to eqns. (11) and (12) on the ionic strength were calculated from the rate constants, k , referring to sodium iodide in Table 1 and values of α obtained by successive approximations ac-

according to Ref. 8 using the ion-pair association constant, $K_A = 13.2 \text{ M}^{-1}$, and the ion-size parameter, $\text{\AA} = 4.7 \times 10^{-8} \text{ cm}$ (Table 3), together with $\epsilon = 27.1$ for the permittivity of the ethanol-water solvent mixture. The value $k_i = 10.72 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ in Table 4 according to the original Acree equation was used for k_i^∞ . This approximation is justified by the fact that the rate constant for reaction of free ions extrapolated to infinite dilution is practically independent of the kinetic salt effect as will be shown below.

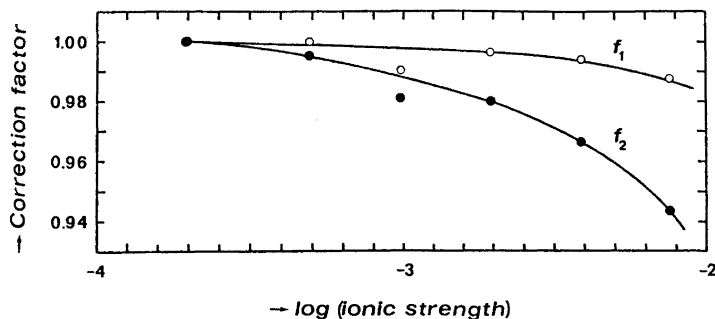


Fig. 1. Minimum and maximum salt effect correction factors, f_1 and f_2 , respectively, as a function of \log (ionic strength).

Table 5. Minimum and maximum salt effect correction factors, f_1 and f_2 , respectively.

$c \times 10^4$ M	$\mu \times 10^4$	f_1	f_2
Potassium iodide			
79.3	74.7	0.988	0.944
39.69	38.22	0.994	0.967
19.82	19.37	0.997	0.980
9.89	9.76	0.998	0.989
4.986	4.950	0.999	0.995
1.995	1.989	1.000	1.000
Rubidium iodide			
78.8	71.1	0.988	0.946
39.56	37.01	0.994	0.968
19.79	19.00	0.997	0.980
9.84	9.61	0.998	0.989
4.951	4.887	0.999	0.995
1.983	1.972	1.000	1.000
Cesium iodide			
39.64	35.96	0.994	0.968
19.95	18.78	0.997	0.980
9.96	9.61	0.998	0.989
4.975	4.878	0.999	0.995
1.991	1.974	1.000	1.000

The results of these calculations are shown graphically in Fig. 1, where f_1 and f_2 , representing minimum and maximum salt effect correction factors, have been plotted on a linear scale as a function of the ionic strength on a logarithmic scale.

Kinetic data from the modified Acree equation. The rate data in Table 1 for the exchange reactions involving potassium, rubidium, and cesium iodide were analyzed as follows by means of the extended Acree equation, eqn. (8).

Values of α for the salt concentrations quoted in the first column of Table 5 were evaluated by successive approximations as above using the association constants and ion-size parameters quoted in Table 3. Subsequently calculated ionic strengths are given in the second column of Table 5 and the corresponding salt effect correction factors, f_1 and f_2 , obtained from the graphs in Fig. 1, are quoted in the last two columns of the same table.

Upon substituting f in eqn. (8) by f_1 or f_2 , respectively, and rearranging the resulting expressions we obtain the following two equations

$$\frac{k}{f_1^\alpha} = k_i^\infty + k_m \frac{1-\alpha}{f_1^\alpha} \quad (13)$$

and

$$\frac{k}{f_2^\alpha} = k_i^\infty + k_m \frac{1-\alpha}{f_2^\alpha} \quad (14)$$

which may be employed to calculate extreme values for k_i^∞ and k_m . Application of the method of least squares yielded the rate constants together with their standard deviations summarized in Table 6.

Table 6. Rate constants, k_i^∞ and k_m , for reactions of unpaired and paired iodide ions evaluated from the Acree equation modified to take into account kinetic salt effect.

Salt	$k_i^\infty \times 10^3$ $M^{-1} s^{-1}$	$k_m \times 10^3$ $M^{-1} s^{-1}$
Minimum salt effect, eqn. (13)		
KI	10.69 ± 0.03	-5.8 ± 1.1
RbI	10.68 ± 0.03	-0.4 ± 0.5
CsI	10.75 ± 0.03	1.8 ± 0.5
Maximum salt effect, eqn. (14)		
KI	10.67 ± 0.03	2.3 ± 1.0
RbI	10.67 ± 0.03	3.9 ± 0.4
CsI	10.73 ± 0.02	4.8 ± 0.4

According to eqn. (13) k_m for the exchange reaction involving cesium iodide is positive and approximately 20 % of k_i^∞ but negative for potassium and rubidium iodide (see the last column in Table 6). The negative values of k_m suggest that the factor, f_1 , according to eqn. (11) underestimates the kinetic salt effect.

All values of k_m derived from eqn. (14) are positive and amount to between 20 and 50 % of k_1^∞ as can be seen in Table 6.

The data in the middle columns of Tables 4 and 6 show that the rate constants k_i and k_i^∞ derived from the original and extended Acree equations differ insignificantly. Compare, for instance, the value $k_i = 10.75 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for the exchange reaction involving cesium iodide according to eqn. (7) with the figures $k_1^\infty = 10.75 \times 10^{-3}$ and $10.73 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ according to eqns. (13) and (14).

Values of k_m are, however, strongly dependent on the salt effect correction. For the cesium iodide exchange reaction $k_m = 1.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ according to eqn. (7) may be compared with the values $k_m = 1.8 \times 10^{-3}$ and $4.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ according to eqns. (13) and (14).

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