Solvent Effects on the Kinetics of Ionic Reactions and the Choice of the Concentration Scale

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(Received May 26, 1942)

The mole fraction scale gives simpler (i.e., more nearly linear) relations between the variables determining kinetics on changing solvents for the bromacetate-thiosulphate reaction than does the usual volume molar scale. The generality and basis of this finding is discussed from the viewpoint of Rabinowitch's cage model theory as well as from that of equilibrium theory. The quenching of fluorescence, which involves diffusion as a rate determining step, is a more nearly linear function of the fluidity when the data are expressed in mole fraction than in the volume molar scale. Experiments are in progress to determine, if possible, whether the cage model or a modified Smoluchowski diffusion treatment fits the facts better for low activation energy reactions like the quenching of fluorescence in solution.

1. INTRODUCTION

SELECTION of the proper concentration scale to be used in comparing either reaction rate or equilibrium constants becomes a problem of importance when the molecular volumes of the solvents differ considerably. For example two bimolecular rate constants which are equal on the mole fraction scale in methyl and in iso-amyl alcohol stand in a ratio of 1 to 3 when compared on a volume molar basis.

In calculating thermodynamic properties, it has been customary to employ the mole fraction scale, whereas in reaction kinetics the universal use of the volume molar scale has not been questioned until recently.[1,2]

It has been suggested that apparent anomalies in the effect of added sucrose and ethanol upon the rate in aqueous solution of the reaction[1,3-7]

$$S_2O_3^= + BrCH_2COO^- = Br^- + CH_2S_2O_3COO^=$$
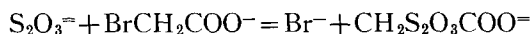
can be eliminated by the conversion of the data from volume molar to mole fraction units.

In order to investigate this suggestion and to attempt to correlate residual and unexplained solvent effects, we have further studied the effect of solvent and of temperature upon this reaction. Data on the solubility of thallous chloride in solvents of differing molecular volume have been obtained for purposes of comparison.

Ions in Solution

Electrostatic theory, applied to a reaction in dilute solution between two ionic reactants A and B of charge Z that form a double-sphere critical complex, leads to the well-known rate equation[8,9]

$$\ln k = \ln k_{D=\infty} - \frac{Z_A Z_B \epsilon^2 N_{Av}}{DRT} \cdot \frac{1}{r_A + r_B} + \frac{Z_A Z_B \epsilon^2 N_{Av}}{DRT} \cdot \frac{\kappa}{1 + \kappa a}, \quad (1)$$

where a is the Debye-Hückel first approximation parameter, $r_A + r_B$ is the separation of the centers of charge in the critical complex, $\kappa = (8\pi\epsilon^2 N_{Av}^2 \mu / DRT 1000)^{\frac{1}{2}}$ from the Debye-Hückel theory,[10] and the other symbols have their usual significance. Analogous equations have been developed from the Debye-Hückel theory for the constants of ionic equilibria. For the solubility of a strong binary electrolyte AB the expression is[9,11]

$$\ln S = \ln S_{D=\infty} - \frac{Z^2 \epsilon^2 N_{Av}}{2DRT}\left(\frac{1}{r_A} + \frac{1}{r_B}\right) + \frac{Z^2 \epsilon^2 N_{Av}}{2DRT} \cdot \frac{\kappa}{1 + \kappa a}. \quad (2)$$

[1] G. Scatchard, J. Chem. Phys. **7**, 657 (1939), discussion by LaMer, p. 662; Ann. N. Y. Acad. Sci. **39**, 341 (1940).
[2] R. P. Bell, Ann. Repts. on Progress of Chemistry **36**, 82 (1939).
[3] LaMer and Kamner, J. Am. Chem. Soc. **57**, 2662 (1935); **57**, 2669 (1935).
[4] Straup and Cohn, J. Am. Chem. Soc. **57**, 1794 (1935).
[5] Tomlinson, Dissertation, Columbia University, N. Y. (1939).
[6] V. K. LaMer, J. Frank. Inst. **225**, 709 (1938).
[7] Kappana, J. Ind. Chem. Soc. **6**, 419 (1929).
[8] Christiansen, Zeits. f. physik. Chemie **113**, 35 (1924).
[9] G. Scatchard, J. Am. Chem. Soc. **52**, 52 (1930); Chem. Rev. **10**, 229 (1932).
[10] Debye and Hückel, Physik. Zeits. **24**, 185 (1923).
[11] Ricci and Davis, J. Am. Chem. Soc. **62**, 407 (1940).

In such equations the logarithm of the constant, or the change in standard free energy of the equilibrium between reactants and critical complex, is expressed as the sum of three terms,[6] the first equal to the value at infinite dielectric constant and thus free of all electrostatic effects; the second, or self-potential term arising from the work of charging the ions in a medium of dielectric constant D; and the third expressing the effect of the ionic atmosphere at an ionic strength μ.

The third term of Eqs. (1) and (2) offers a simple method of extrapolation to infinite dilution ($\kappa = 0$), by a suitable choice of the parameter a. When the simple Debye-Hückel theory cannot be applied, this term may be modified by use of the idea of ion-association,[12,13] but the extrapolation is often unsatisfactory.

Both Eqs. (1) and (2) predict that the plot of $\log k_{\kappa=0}$ or $\log S_{\kappa=0}$ vs. $1/D$ will be linear. The value of $r_A + r_B$ or $1/r_A + 1/r_B$ can be determined from the slope. Such a linear plot is often found, but there are serious objections to the literal interpretation of the self-potential term: the value of $r_A + r_B$ is often either too large or too small for the physical model[14,15] and may even be negative; it is in general dependent on both temperature and solvent; the use of the macroscopic dielectric constant has long been considered questionable, since the orientation of the solvent dipoles in the field of the ions will make the effective dielectric constant lower.[16] The plot of $\log k_{\kappa=0}$ vs. $1/D$ is not always linear and indeed always shows curvature at sufficiently low dielectrics. Imperfect extrapolation to zero ionic strength is an important cause of such curvature, but there is reason to suspect that even when the extrapolation is valid, a linear plot may not always be obtained.

## The Normalized Mole Fraction Rate Constant

Conversion of a second-order reaction rate constant k from volume-molar units, liters per mole, to mole fraction units, total moles per mole, requires multiplication by the factor, total moles per liter. If the mole fraction constant is divided by the total number of moles per liter in a standard solvent, a normalized constant, k^N, is obtained. This is proportional to the mole fraction constant, but becomes equal to the volume molar constant when the standard solvent is used.[1]

$$k^N = k \frac{\sum \text{Moles/liter}}{\sum (\text{Moles/liter})_{\text{standard}}}. \quad (3)$$

Water at $4°$, with 55.5 moles per liter, has been chosen as the standard solvent to which the data of this paper on the bromacetate-thiosulfate reaction have been referred.

Consider a reaction of the type

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} X \overset{k_3}{\rightarrow} \text{Products},$$
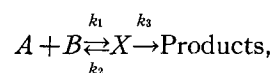
where X denotes the critical complex. Let K_X be the equilibrium constant $(N_X/N_A N_B)(\gamma_X/\gamma_A \gamma_B)$ of the former equilibrium, $N =$ mole fraction and $\gamma =$ mole fraction activity coefficient, and let the rate determining step of the over-all reaction be the unimolecular decomposition of the critical complex:

$$-\frac{d[X]}{dt} = k_3[X] = k_3 K_X \frac{N_A N_B}{N_X} \frac{\gamma_A \gamma_B}{\gamma_X}[X]. \quad (4)$$

$$k = \text{Molar rate constant} = \frac{-d[X]/dt}{[A][B]}$$

$$= k_3 K_X \frac{\gamma_A \gamma_B}{\gamma_X} \frac{N_A}{[A]} \frac{N_B}{[B]} \frac{[X]}{N_X}$$

$$= k_3 K_X \frac{\gamma_A \gamma_B}{\gamma_X} \left(\sum \frac{\text{moles}}{\text{liter}}\right)^{(1-m)}, \quad (5)$$

where $m = 2$ is the total number of reactants. Generalizing the definition of K^N (Eq. (3)), we have

$$k^N = k \frac{\left(\sum \dfrac{\text{moles}}{\text{liter}}\right)^{(m-1)}_{\text{solvent}}}{\left(\sum \dfrac{\text{moles}}{\text{liter}}\right)^{(m-1)}_{\text{standard}}}$$

$$= k_3 K_X \frac{\gamma_A \gamma_B}{\gamma_X \left(\sum \dfrac{\text{moles}}{\text{liter}}\right)^{(m-1)}_{\text{standard}}}. \quad (6)$$

[12] Bjerrum, K. Danske Vidensk. Selskab, **7**, No. 9 (1926).
[13] Hogge and Garrett, J. Am. Chem. Soc. **63**, 1089 (1941).
[14] Amis and LaMer, J. Am. Chem. Soc. **61**, 905 (1939).
[15] Amis, J. Am. Chem. Soc. **63**, 1606 (1941).
[16] H. Frank, J. Am. Chem. Soc. **63**, 1789 (1941).

Since k_3 has the dimensions of frequency, we denote it by the symbol ν. If K_x is replaced by its thermodynamic equivalent, Eq. (5) becomes for a bimolecular reaction

$$k = \nu e^{-\Delta H_0^{\ddagger}/RT} e^{\Delta S_0^{\ddagger}/R} \frac{\gamma_A \gamma_B}{\gamma_X} \left(\sum \frac{\text{moles}}{\text{liter}} \right)^{-1}. \quad (7)$$

The corresponding Eyring absolute rate equation for a bimolecular reaction in solution is[17]

$$k = e \frac{RT}{Nh} e^{-\Delta E_{exp}/RT} e^{\Delta S^{\ddagger}/R} \frac{\gamma_A \gamma_B}{\gamma_X} \left(\sum \frac{\text{moles}}{\text{liter}} \right)^{-1}, \quad (8)$$

where ΔE_{exp} or E_{act} is obtained from the slope of $\log k$ vs $1/T$ and where we have added the activity coefficient term and imply a mole fraction equilibrium constant K_x.

Using the "cage model" of a liquid, Rabinowitch[18,19] has developed an improved collision theory of bimolecular reaction rates in solution. His equation is

$$k = n \frac{N_{Av}}{N_0} \nu e^{-E_{act}/RT} \bigg/ \left(1 + \frac{a^2 \gamma_1}{4D_i} \nu e^{-E_{act}/RT} \right), \quad (9)$$

in which n is the coordination number (effective for reaction) of a reactant molecule, N_0 is the number of liquid lattice points per liter, a is the "lattice distance," D_i is an average diffusion coefficient of the reactants, ν is a frequency characteristic of the solvent, γ_1 is a factor accounting for the fact that a "jump" of molecule B may not destroy coordination with molecule A, and the other symbols have their usual significance.

Equation (9) shares with earlier collision equations based on gas kinetics the disadvantage of neglecting the entropy factor exp $\Delta S^*/R$ arising from the internal degrees of freedom of the molecules concerned. It is nevertheless valuable because of the clear picture it gives of the significance of a "collision" and of the positional condition for reaction; namely, that two molecules must be in a state of coordination in order to react. Equation (9) also distinguishes clearly

reactions with negligible energy of activation, and an observed dependence on viscosity from the commonly studied reactions with appreciable energy of activation and no observable dependence on viscosity. If E_{act} is small, the equation reduces to

$$k = 4n N_{Av} D_i / N_0 a^2 \gamma_1 \quad (10)$$

and for larger values of E_{act}, to

$$k = \frac{n N_{Av}}{N_0} \nu e^{-E_{act}/RT}. \quad (11)$$

If N_0 is equal to the total number of all molecules per liter and if n remains constant, the simple Eq. (11) predicts that k^N will be independent of solvent.

As it stands, Eq. (11) is evidently incompatible with Eqs. (5), (7), and (8). Arbitrary insertion into Eq. (11) of the missing entropy and activity coefficient factors, which must be found in any acceptable equation, gives

$$k = n \frac{N_{Av}}{N_0} \nu e^{-E_{act}/RT} e^{\Delta S^{\ddagger}/R} \frac{\gamma_A \gamma_B}{\gamma_X}. \quad (12)$$

Comparison of Eqs. (12) and (7) clarifies the significance of the mole fraction rate equation in terms of collisions. If the total number of lattice positions per unit volume, N_0, were a constant independent of the solvent, Eq. (12) would be essentially the usual volume molar rate equation. When however rate constants in solvents of differing molecular volume are compared in mole fraction units, the tacit assumption is made that the total number of molecules per liter present, the total number of positions in the liquid lattice, and the effective number of lattice positions for the reactant molecules are equal to each other. With these assumptions, Eq. (12) becomes essentially identical with Eq. (7).

Temperature Coefficients of Ionic Reactions

The energy and entropy of activation of an ionic reaction, calculated in the usual way at constant solvent composition, are functions of dD/dT for the particular solvent used.[6,14,20,21] It

[17] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (The McGraw-Hill Book Company, New York, 1941), p. 199.
[18] Rabinowitch, Trans. Faraday Soc. **33**, 1225 (1937); Rabinowitch and Wood, *ibid.* **32**, 1381 (1936).
[19] Mark and Simha, Naturwiss. **25**, 833 (1937).

[20] Svirbely and Warner, J. Am. Chem. Soc. **57**, 1883 (1935).
[21] Warner, Ann. N. Y. Acad. Sci. **39**, 345 (1940).

has been pointed out that according to Eq. (1) the effect of electrostatic forces on the temperature coefficient may be removed by extrapolating log k to infinite dielectric constant, $1/D = 0$. Thus values of the entropy, $\Delta S^{\ddagger}$, and energy, $\Delta E^{\ddagger}$, of activation may be obtained, which are independent of the ionic properties of the reactants. Consideration of Eq. (1) suggests that the value of the entropy of activation so obtained is equivalent[6,20,21] to the so-called isodielectric entropy of activation, $\Delta S^{\ddagger}_{\text{const } D}$ obtained by arbitraily varying the composition of the solvent in such a manner as to maintain the dielectric constant independent of temperature.

Moreover, we note that by varying the solvent composition in such a way that the product DT is maintained constant, it is possible according to Eq. (1) to obtain a temperature coefficient and therefore an energy of activation, $\Delta E^{\ddagger}_{\text{const } DT}$ independent of the electrostatic terms and equal to $\Delta E^{\ddagger}_{D=\infty}$.

In this case it is not necessary to compare results at zero ionic strength, but only at constant concentration of reactants, provided that the rate constant is separable into three terms as in Eq. (1) and that the ionic atmosphere term involves D and T only as the product; this is true not only of Eq. (1) but of all equations derived from the Debye-Hückel postulates, such as those of Bjerrum[12] and of Gronwall, LaMer, and Sandved.[22]

When the temperature coefficient is measured with D held constant, the entire electrostatic effect is arbitrarily thrown into the energy of activation, $\Delta E^{\ddagger}_{\text{const } D}$. Likewise when the product DT is held constant the electrostatic effect is arbitrarily absorbed in the entropy term, $\Delta S^{\ddagger}_{\text{const } DT}$.

Equation (1) predicts that $\Delta S^{\ddagger}_{\text{const } D}$ and $\Delta E^{\ddagger}_{\text{const } DT}$ will be independent of dielectric constant and of solvent. Failure to find such an independence may be taken as indicative of the importance of solvent effects not accounted for by an equation derived from simple electrostatic postulates alone. In particular the consideration of $\Delta E^{\ddagger}_{\text{const } DT}$ may help to determine the relative importance of electrostatic and non-electrostatic effects even when a satisfactory extrapolation to zero ionic strength cannot be made. If $\Delta S^{\ddagger}_{\text{const } D}$ and $\Delta E^{\ddagger}_{\text{const } DT}$ really approximate closely the values for the reaction freed of electrostatic effects, they may be expected to be practically temperature independent.

NEW EXPERIMENTS ON BROMACETATE-THIOSULFATE REACTION

A. Materials

Bromacetic acid was purified by fractional crystallization, sublimation under reduced pressure, and drying over sulfuric acid. Determinations of acidity and of bromine agreed with calculated values within 0.1 percent.

C.P. methanol was distilled over sodium and silver nitrate. Concentration of solution was checked by density measurements.

Glycine was purified by precipitation with alcohol from the aqueous solution, followed by three recrystallizations from water. A $1M$ solution had a conductivity of 9×10^{-6} mho and a pH of about 5.9.

Atlas commercial d-mannitol was recrystallized twice from water. Melting point 165.9°.

Dioxane and t-butanol were purified as described by Tomlinson,[5] t-butanol receiving two redistillations.

Ethylene glycol was stored for several days over calcium oxide and distilled under reduced pressure.

Clear potato starch solution (about 0.1 percent) was used as an indicator in iodine titrations. The sensitivity of the end point was roughly 10^{-7} mole per liter of iodine when $D > 70$.

Thallous chloride was purified and prepared as described by Hogge and Garrett.[13]

Analytical reagent potassium iodate, used as a primary standard, was recrystallized, ground and dried at 150°. C.P. sucrose and neutral potassium iodide were used.

B. Methods

The experimental methods are those previously described by LaMer and Kamner[3] and Tomlinson[5] except as follows:

Reactions in high dielectric solvents were stopped by dilution and cooling with a mixture of starch solution and chopped ice, followed by immediate titration from a weight burette. Re-

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[22] Gronwall, LaMer, and Sandved, Physik. Zeits. **29**, 558 (1928).

actions in solvents of dielectric constant lower than 40 were stopped by addition of a measured amount of iodine solution from a carefully calibrated hypodermic syringe. The small excess of iodine was determined by measuring the transmittance of the solution at $\lambda = 3650\text{A}$ with a Coleman spectrophotometer and comparing with a previously prepared curve, or by titration with dilute thiosulfate to 100 percent transmittance. The two methods gave identical results.

When either dioxane or glycine was the added solvent, a sodium thiosulfate solution in this mixture, containing any added lanthanum chloride, was mixed at zero time with a smaller quantity of a stronger sodium bromacetate solution in water only, without added solvent. This precaution was taken to avoid peroxide formation in dioxane and hydrolysis of bromacetate ion in the presence of glycine.

In glycine solutions it was important to add a little $0.1N$ acetic acid to the reaction mixture before titration.

The method of Hogge and Garrett[13] was employed in following thallous chloride solubilities.

The temperature of thermostats was determined to within $0.02°$ by means of a platinum resistance thermometer.

Values of the dielectric constant of glycine solutions have been specially re-determined for us by Dr. Jeffries Wyman, Jr.[23] Other values have been taken from the literature.[24]

C. Results

Data are presented in Table I for the bromacetate-thiosulfate reaction in water, glycine-water, methanol-water, and sucrose-water at 25° and 45° and for t-butanol-water, glycol-water, and mannitol-water at 25°; in the lower dielectric range constants have been obtained in t-butanol-water, dioxane-water mixtures at 25° and 45° and in dioxane-water with added lanthanum chloride (Table II). In glycine solutions at 45° a small drift with time was observed, which was apparently caused by a glycine catalyzed hydrolysis of bromacetate ion. A short extrapolation to zero time, the uncertainity of which is less than 1 percent, surmounted this difficulty. The drift can

[23] Wyman, in press.
[24] Åkerlof, J. Am. Chem. Soc. **54**, 4125 (1932); Åkerlof and Short, *ibid.* **58**, 1241 (1936).

TABLE I. Summary of data in high dielectric solvents.

Solvent	D	$\sqrt{\mu}$	k	$\log k_{K=0}+1$	$1+\log k^N_{K=0}$
		$T=25°C$	$a=6.4\text{A}$		
16% Sucrose	74.7	0.1299	0.406	0.387	0.343
10% MeOH	74.1	.0815	.3220	.355	.327
20% MeOH	69.2	.0616	.2713	.302	.247
35% MeOH	61.9	.1446	.3337	.212 ⎫	
35% MeOH	61.9	.1238	.308	.212 ⎬	.098
35% MeOH	61.9	.0914	.269	.213 ⎭	
8% t-Butanol	71.8	.0730	.3174	.356	.323
16% t-Butanol	64.9	.1460	.4127	.323 ⎫	
16% t-Butanol	64.9	.1333	.3934	.320 ⎬	.255
16% t-Butanol	64.9	.1090	.322	.322 ⎭	
14.7% mannitol	76.4	.1390	.4265	.405 ⎫	
14.7% mannitol	76.4	.1032	.381	.403 ⎬	.363
14.7% mannitol	76.4	.0945	.371	.404 ⎭	
26.4% glycol	70.9	.1660	.4630	.379	.305
2.309M glycine	131.5	.1666	1.021	.887	.857
2.309M glycine	inf.	extrapolated*			1.519
		$T=45°C$	$a=6.8\text{A}$		
Water	71.66	0.1701	2.406	1.1226	
Water	71.66	.1722	2.413	1.1213	
Water	71.66	.2178	2.677	1.1183	
Water	71.66	.2639	2.954	*1.1223*	
Water	71.66	mean		1.1216	1.118
0.363M glycine	79.55	0.1991	3.101	1.234	1.225
1.00M glycine	93.37	.1412	3.54	1.394	
					1.379
1.00M glycine	93.37	.2447	4.25	1.395	
2.294M glycine	121.5	.1660	5.51	1.618	1.585
glycine	inf.				2.254
17.3% MeOH	63.8	.1988	2.276	1.019	0.962
31% sucrose	63.8	.1467	2.153	1.061	.960

* Compare Table III.

be accounted for by postulation of a side reaction, second order in bromacetate ion and glycine, with a specific rate constant of 5×10^{-4} liter per mole per minute.

Recalculated data of LaMer and Kamner,[3] Straup and Cohn,[4] and Tomlinson[5, 6] are given in Table III. The data of Kappana[7] cannot be interpreted consistently and in particular his constants obtained in sucrose-water and ethanol-water mixtures cannot be extrapolated accurately to zero ionic strength, and are in disagreement with other work. They have, therefore, been omitted.

In Table IV are listed a few new determinations of the solubility of thallous chloride, together with some values from the literature.

DISCUSSION

A. The Bromacetate-Thiosulfate Reaction

In Figs. 1 and 2 $\log k_{K=0}$ for the bromacetate-thiosulfate reaction is plotted against the reciprocal of the dielectric constant, with k calculated in 1 in the usual volume molar units, liters per mole per minute, and in 2 in the normalized mole fraction units of Eq. (3). The points obtained in glycine-water solutions lie on a straight line in both plots at 45° and 25°. When the solvents are

TABLE II. Summary of data obtained in low dielectric solvents.

D	$C_{LaCl_3}=0.642 \times C_{Na_2S_2O_3}$ $t=25°C$ Concentration $M/1 \cdot 10^4$	k_{-1} (min.$^{-1}$)	Dioxane-water mixtures $\log \frac{M/l}{55.5}$	$\log k^N$
20.4	3.963	201.8	0.312	1.993
25.0	3.981	135.9	.275	1.858
29.7	3.984	90.8	.237	1.721
34.8	3.980	58.6	.203	1.565
		$t=45°C$		
20.2	3.920	873		
			0.299	2.643
20.2	3.907	878		
22.3	3.907	725	.280	2.580
30.1	3.895	363		
			.209	2.347
30.1	3.915	356		
		No LaCl$_3$ $t=25°C$		
20.1^a	4.034	0.702	0.314	1.533
23.3^b	20.95	.895	.373	1.579
25.3^b	50.05	1.035	.349	1.666
		$t=45°C$		
20.0^a	3.958	2.98	0.301	0.173
20.0^b	20.55	4.93	.381	.312
21.8^b	20.17	3.96	.357	.241
21.8^b	49.58	5.67	.357	.397
23.2^b	49.58	5.09	.339	.368

^{a} Dioxane water. ^{b} t-Butanol water.

TABLE III. Summary of data recalculated and used for curves. $T=25°C$.

Observer	Solvent	D	$1+\log k_{K=0}$	$1+\log k_{K=0}^N$
K, F	water	78.54	0.399	0.398
K	1.47% sucrose	78.2	.401	.398
K	32.4% "	70.2	.368	.266
K	67.9% glycerol	56.5	.286	.012
K	3.73 M urea	88.4	.555	.508
S	2.00 M "	84.0	.478	.453
S	4.00 M "	89.0	.557	.506
S	5.00 M "	91.0	.584	.520
S	0.40 M glycine	87.7	.522	.516
S	0.62 M "	92.7	.577	.567
S	1.00 M "	101.4	.669	.655
S	1.70 M ethanol	74.0	.362	.333
S	3.41 M "	69.2	.334	.276
S	5.11 M "	64.3	.308	.220
T	2.60 M glycine	138.1	.903	.869
T	2.80 M "	142.6	.917	.880

K—Kamner, reference 3.
S—Straup, reference 4.
F—Fessenden [LaMer and Fessenden, J. Am. Chem. Soc. 54, 2351 (1932)].
T—Tomlinson, reference 5.

aqueous mixtures of dielectric constant lower than that of water, a linear plot may or may not be obtained: if methanol-water solutions are used, the points obey the linear relation of Eq. (1) within the experimental error; if tertiary butanol

is the added solvent, there is a slight upward curvature.

Comparison of Figs. 1 and 2 demonstrates that use of a mole fraction scale effectively eliminates most of the specific solvent differences evident in Fig. 1. The points obtained in water and in mixtures of water with glycine, sucrose, mannitol, or methanol are collinear after normalization; those obtained when the added solvent is ethanol, glycol, or glycerol show a slight deviation, while the points obtained in t-butanol-water mixtures lie appreciably above the others, but are much closer to the extrapolated high dielectric curve than when plotted on the volume-molar scale. The correction on the urea-points is too large, so that these lie below the common linear plot of Fig. 2. The values of the parameter, r_A+r_B, calculated from Figs. 1 and 2, (Table V) clearly illustrate the above conclusions.

While isodielectric methanol-water and sucrose-water solutions are, when k^N is used, equivalent solvents at 45° as at 25°, there remains a definite difference in the slopes of $\log k_{K=0}^N$ vs. $1/D$ above and below the water point at the higher temperature. The value of r_A+r_B obtained from the high dielectric curve does not change significantly between 25° and 45°, while the value calculated from the sucrose-water points shows some temperature dependence. Such a temperature dependence suggests the existence of solvent effects not accounted for by Eq. (1) and not entirely removed by the use of k^N. The parameter r_A+r_B is a convenient catch-all for such effects.

A linear relation between $\log k_{K=0}^N$ and $1/D$ does not disprove the existence of non-electrostatic effects. $1/D$ is very nearly linear in the mole fraction of such solvents as methanol,

TABLE IV. Solubility of thallous chloride.

Solvent	D	Solubility (moles/l)	Solubility $\times \frac{55.3}{\Sigma \text{ moles/l}}$
H$_2$O (reference 13)	78.54	0.01617	0.01617
H$_2$O	78.54	.01617	.01617
16% d-mannitol	76.1	.01688	.01869
8.3% glycol	76.1	.01530	.01613
2.7% t-butanol	76.1	.01466	.01494
5.5% methanol	76.1	.01373	.01419
4.2% ethanol (reference 13)	76.1	.01405	.01437
0.5 M glycine	89.99	.01893	.01923
D$_2$O*	78.3	.01213	.01217

* Kingerley and LaMer, J. Am. Chem. Soc. 63, 3256 (1941).

sucrose, glycol, ethanol, etc. (but not t-butanol) added to water, over a range from 0–40 percent or more. If there is a specific solvent effect, also linear in the mole fraction of added solvent, the plot of log $k_{\kappa=0}^N$ vs. $1/D$ may still be straight. The values of log $k_{D=\infty}$ and r_A+r_B obtained will, however, be in error and in general dependent on both solvent and temperature. The low and solvent-dependent values of r_A+r_B obtained from the kinetics of carbinol formation of dye ions[14, 25] are apparently at least partly caused by such a linear solvent effect.

The data of Table I indicate that the Debye-Hückel extrapolation to zero ionic strength can be made satisfactorily when $D>60$. It seems likely, therefore, that the deviations from linearity in this range (Fig. 2) cannot be explained as the result of ion-association alone.

Tables VI and VII contain values of the energies and entropies of activation and of the "frequency factor" log B calculated from the Arrhenius equation and Eq. (8) using the data of Tables I, II and III and Figs. 2 and 3. A number of conclusions may be drawn:

In media of high dielectric constant the iso-dielectric B and $\Delta S^\ddagger$ are practically independent of D, T, or solvent used, whereas the constant composition B and $\Delta S^\ddagger$ decrease as D decreases. This decrease corresponds to a lowered probability of coordination of the like-charged reactant ions.

$\Delta E^\ddagger$ is temperature dependent when measured at constant composition, has a very slight dependence when measured in isodielectric media, and is practically independent of temperature when measured with the product DT held constant.

TABLE V. Values of slope log $k_{\kappa=0}$ vs. $1/D$.

$T°C$	Added solvent	Conc. scale	Slope	r_A+r_B (A)
25	glycine, sucrose, methanol, mannite	Normalized	−87.8	5.55
25	urea	Normalized	−69.1	7.04
45	glycine	Normalized	−81.4	5.62
45	sucrose, methanol	Normalized	−90.2	5.06
0	sucrose	Normalized	−75.8	6.43
25	mannitol	vol. molar	+18	−27
25	sucrose	vol. molar	−20.6	+23.6
25	t-butanol	vol. molar	−28.2	17.3
25	methanol	vol. molar	−54.9	8.9
25	glycine	vol. molar	−94.0	5.18
45	sucrose	vol. molar	−35.3	12.9
45	methanol	vol. molar	−59.5	7.7
45	glycine	vol. molar	−91.3	5.34
0	sucrose	vol. molar	−13.8	39

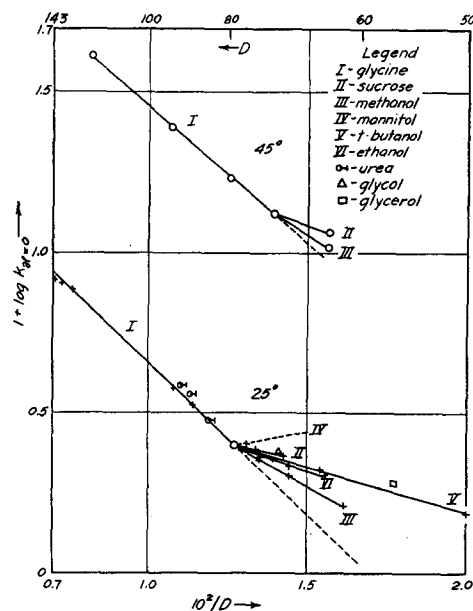[25] Hochberg and LaMer, J. Am. Chem. Soc. **63**, 3110 (1941).

FIG. 1. Volume molar rate constant $k_{\kappa=0}$ (in min.$^{-1}$) for bromacetate-thiosulfate reaction as function of temperature and dielectric constant.

$\Delta S^\ddagger$, calculated from the data for the lanthanum ion catalyzed reaction at a low constant ionic strength with dielectric constant of 20 to 35, decreases in absolute value (becomes less negative) as D decreases. This corresponds to a negative ionic strength effect consistent with
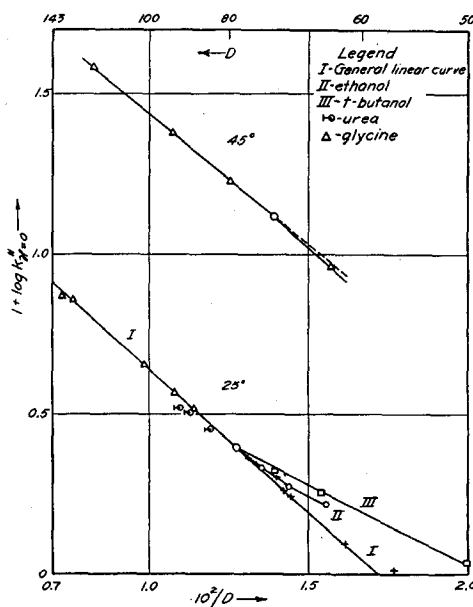

FIG. 2. Normalized mole fraction rate constant $k_{\kappa=0}^N$ (in min.$^{-1}$) for bromacetate-thiosulfate reaction as function of temperature and dielectric constant.

TABLE VI. Energies and entropies of activation in media of high dielectric constant. k^N(min.$^{-1}$) $\kappa = 0$.

Range	Solvent added to water	$D(25°)$	$\Delta E^{\ddagger}$	$\log_{10} B$	$-\Delta S^{\ddagger}$ cal./deg.
		Constant Composition			
0–25°	none	78.54	15,730	10.94	18.5
0–25°	32.4% sucrose	70.2	15,530	10.64	19.9
25–45°	none	78.54	15,640	10.94	18.7
25–45°	32.4% sucrose	70.2	14,850	10.19	22.1
25–45°	17.3% methanol	70.5	14,980	10.26	21.8
25–45°	1M glycine	101.4	15,660	11.12	17.8
25–45°	2.3M glycine	131.3	15,850	11.47	16.2
		Constant Dielectric			
0–25°	glycine	88.06	17 530	12.35	12.1
0–25°	sucrose	78.54	17,530	12.26	12.5
25–45°	glycine	78.54	17,720	12.38	12.1
25–45°	glycine	88.06	17,530	12.36	12.2
25–45°	sucrose-methanol	71.66	17,920	12.41	11.9
25–45°	t-butanol	71.66	17,270	11.97	14.0
25–45°	glycine	inf.	15,960	12.23	12.8
		Constant (DT)			
0–25°	glycine	80.67	16,180	11.30	16.9
0–25°	sucrose	71.9	16,030	11.05	18.0
25–45°	glycine	78.54	16,200	11.27	17.2
25–45°	sucrose	70.2	16,170	11.14	17.7
25–45°	glycine	inf.	15,960	12.23	12.8

previous conclusions[5, 6] that the reaction is between the positive complex ion La$^{+++} \cdot$S$_2$O$_3^=$ and the negative BrAc$^-$. $\Delta E^{\ddagger}_{\text{const }D}$ is independent of dielectric constant, while $\Delta E^{\ddagger}_{\text{const }DT}$ decreases slightly as D decreases. This might be caused by a positive non-electrostatic effect and a corresponding dependence of parameters on temperature.

When no lanthanum chloride is added a value of $\Delta E^{\ddagger}_{\text{const }DT}$ is obtained (Table VII) almost identical with that obtained for the catalyzed reaction. From this we conclude that the great increase in the reaction rate when lanthanum ion is present is purely an electrostatic effect. The value of $\log B_{\text{const }DT}$, on the other hand, is over two units higher for the catalyzed reaction.

$\Delta E^{\ddagger}_{\text{const }DT}$ is about 1000 cal. lower in the low dielectric media than in the high dielectric media studied. This indicates that there may be an important positive non-electrostatic effect in the dioxane-water and t-butanol-water mixtures and that the upward curvature of the plot of $\log k$ vs. $1/D$, found by Tomlinson[5, 6] is not due entirely to the uncertainty of the extrapolation to zero ionic strength.

If the value of nN_{Av}/N_0 in Eq. (12) is taken as $1/55.5$, and the entropy factor is taken as one, the value of the isodielectric frequency factor B calculated is only about 0.0–0.6 log unit larger than that experimentally obtained, whereas Eyring's estimates from the transition state

theory[26] for two reacting polyatomic molecules call for an entropy factor of 10^{-5}–10^{-10}. This apparent disagreement is typical of reactions involving ions and is presumably the result of large entropies of vaporization and large solvent and solvation effects. The agreement with predictions of the collision theory is probably quite fortuitous; for many non-ionic reactions and for some ionic reactions (see, for example, reference 25) it is very poor.

B. Effect of Choice of Concentration Scale upon Interpretation of Other Reaction Rates

Search of the literature reveals some previous data, the interpretation of which might be affected by a change to the mole fraction concentration scale. Two interesting cases are discussed in Sections (C) and (D). Straup and Cohn[4] have studied the bromacetate-thiosulfate reaction in mixtures of water, ethanol, and either glycine or urea, iso-dielectric with water, with results consistent with those already discussed; the mole fraction constant is about the same in the isodielectric solvents, but appreciably low in the urea mixtures.

For a reaction between *an ion* and *a neutral molecule*, the importance of the dielectric constant will depend upon the geometry of the critical complex. If the reactants can be considered as two particles approaching each other and forming

TABLE VII. Energies and entropies of activation in media of low dielectric constant. k^N in min.$^{-1}$, $t = 25° - 45°$.

Solvent added to water	Concentration of reactants	D	$\Delta E^{\ddagger}$	$\log B$ (min.)$^{-1}$	$-\Delta S^{\ddagger}$ cal./deg.
		Constant Composition			
49.43% dioxane; LaCl$_3$	3.9	34.8	16,980	14.03	4.5
61.09% dioxane; LaCl$_3$	3.9	25.0	15,720	13.38	7.8
63.80% dioxane; LaCl$_3$	3.9	22.7	15,640	13.37	7.9
66.50% t-butanol; No LaCl$_3$	20.5	23.3	15,960	11.29	17.1
63.80% t-butanol; No LaCl$_3$	50.5	25.3	15,890	11.34	16.8
		Constant Dielectric			
dioxane; LaCl$_3$	3.9	20.2	13,960	12.21	12.8
dioxane; LaCl$_3$	3.9	22.3	14,000	12.19	12.9
dioxane; LaCl$_3$	3.9	25.0	13,940	12.04	13.6
dioxane; LaCl$_3$	3.9	30.1	13,940	11.92	14.2
dioxane; No LaCl$_3$	3.9	20.0	13,810	9.66	24.5
t-butanol; No LaCl$_3$	20.5	23.3	13,370	9.36	25.9
		Constant (DT)			
dioxane; LaCl$_3$	3.9	32.1	15,230	12.78	10.3
dioxane; LaCl$_3$	3.9	26.7	14,970	12.77	10.3
dioxane; LaCl$_3$	3.9	23.8	14,990	12.86	9.9
dioxane; LaCl$_3$	3.9	21.6	14,900	12.86	9.9
t-butanol; No LaCl$_3$	20.5	23.3	14,480	10.18	22.2
t-butanol; No LaCl$_3$	50.5	25.3	15,070	10.70	19.8

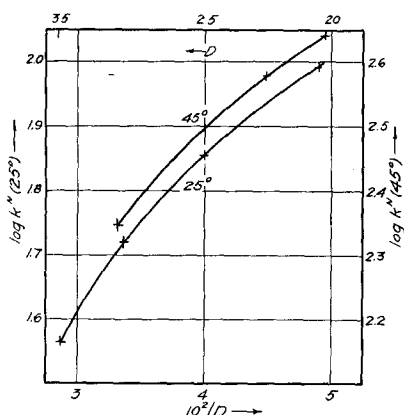[26] Glasstone, Laidler, and Eyring, reference 17, p. 19.

FIG. 3. Effect of dielectric on La^{+++} catalyzed reaction.

a double-sphere critical complex such as that of Eq. (1), with the charge continuing to be centered on the reacting ion, little effect will be expected. This is an extreme case. The opposite extreme, in which the critical complex can be represented as a single sphere with the charge symmetrically distributed about its center leads to the equation[27]

$$\ln k_{\kappa=0} = \ln k_{D=\infty} + \frac{Z_A{}^2 \epsilon^2 N_{Av}}{2DRTr_A} - \frac{Z_A{}^2 \epsilon^2 N_{Av}}{2DRTr_X}. \quad (13)$$

Since r_x is greater than r_A Laidler and Eyring conclude that the rate of a reaction between an ion and a neutral molecule should increase with decreasing dielectric constant.

As the actual case probably lies somewhere between these extremes, Eq. (13) should predict a self-potential effect of the right sign but too large. The experimental examples suggested[27,28] are not entirely convincing. The supposed dielectric constant effect on the reactions between water and a sulfonium cation[29] and between alkyl halides and halide ions[30] is so large that one suspects other effects may be very important. On the other hand, the reaction between hydroxyl ion and isopropyl bromide, studied[31] in 60 percent and 80 percent ethanol solutions is significantly faster in

[27] Laidler and Eyring, Ann. N. Y. Acad. Sci. **39**, 303 (1940).
[28] Glasstone, Laidler, and Eyring, reference 17, p. 439 seq.
[29] Hughes and Ingold, J. Chem. Soc. (London), 1571 (1933).
[30] Bergmann, Polanyi, and Szabo, Zeits. f. physik. Chemie **B20**, 161 (1933).
[31] Hughes, Ingold, and Shapiro, J. Chem. Soc. (London), 225 (1936).

the latter solvent only when volume molar concentration units are used. On a mole fraction basis the "effect" will evidently become of the wrong sign at a temperature slightly below those used for the measurements (Table VIII). Probably no definite conclusions as to the importance of dielectric constant effects should be drawn until it is possible to separate the non-electrostatic effects.

There are, however, at least two similar cases in which this can be accomplished in part. The increase of the rate of reaction between thiosulfate ion and methyl bromacetate[5,6] when t-butanol is added to the water-solvent, is more than removed by conversion to a mole fraction scale. Comparison with the observed solvent effects on the corresponding reaction with bromacetate ion suggests that in this case the self-potential effect is unimportant. The reaction between alkyl halides and thiosulfate ion has been studied[4] in water, in mixtures of water with ethanol, glycine, and urea, and in mixtures of water, ethanol, and either glycine or urea isodielectric with water (Table IX). The results indicate a small self-potential effect of the sign predicted by Eq. (12) when glycine or urea is added, although this is only evident in the latter case when the mole fraction scale is used. When ethanol is the added solvent a similar effect appears to be present, but is far less important than another solvent effect.

C. The Quenching of Fluorescence

The quantity $(I_0/I-1)/C_Q = k_Q$ is obtained[32] from studies of the quenching of fluorescence in solution. I_0 is the intensity of fluorescent light emitted by a solution before addition of a

TABLE VIII. Effect of solvent upon reaction between isopropyl bromide and hydroxyl ion, from data of Hughes, Ingold, and Shapiro, reference 31.

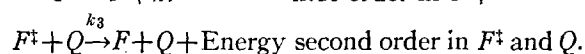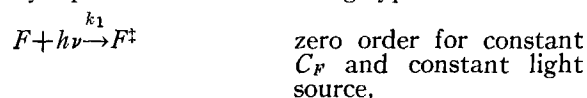| $t°C$	Medium	D	k	k^N (60% ethanol)
80	80% Ethanol	23.20	4.61	3.52
80	60% "	31.82	3.11	3.11
50	80% "	28.10	0.241	0.184
50	60% "	37.72	.181	.181
35	80% "	30.8	.0477*	.0345*
35	60% "	41.1	.0368*	.0368*

* Values obtained by extrapolation.

[32] Wawilow and Frank, Zeits. f. Physik **69**, 100 (1931).

TABLE IX. Effect of solvent upon reaction between methyl iodide and thiosulfate ion, from data of Straup and Cohn, reference 4. $CH_3I+S_2O_3^- \rightarrow CH_3S_2O_3^- + I^-$. $t = 25°C$.

Medium	D	$\log k - \log k_{H_2O}$	$\log k^N - \log k_{H_2O}$
20% ethanol	69.5	0.241	0.183
0.4M glycine in 20% ethanol	78.5	.204	.141
0.4M glycine	87.7	− .054	− .060
30% ethanol	64.5	+ .395	+ .307
0.62M glycine in 30% ethanol	78.5	+ .241	+ .145
0.62M glycine	92.7	− .74	− .75
5M urea in 30% ethanol	78.5	+ .353	+ .21
5M urea	91.0	+ .022	− .042

quenching material and I is the intensity at a concentration C_Q of quencher. A constant source of illumination is used, and the molar concentration of fluorescent material is in general much smaller than that of quencher. To show that k_Q is proportional to the second-order rate constant for the quenching reaction, we need make no assumptions concerning the mechanism[32-35] beyond that the process of activation of a molecule F by a light source, the emission of fluorescent light, and the deactivation of an activated molecule by a quenching molecule may be represented by equations of the following type:

$$F + h\nu \xrightarrow{k_1} F^{\ddagger}$$

zero order for constant C_F and constant light source,

$$F^{\ddagger} \xrightarrow{k_2} F + h\nu$$

first order in $F^{\ddagger}$,

$$F^{\ddagger} + Q \xrightarrow{k_3} F + Q + \text{Energy}$$ second order in $F^{\ddagger}$ and Q.

Since I is independent of time a steady state exists.

$$dC_F^{\ddagger}/dt = 0 = k_1 - k_2 C_F^{\ddagger} - k_3 C_F^{\ddagger} C_Q. \quad (14)$$

We choose the units of k_1 and k_2 so that I and I_0, in Einsteins per second, are given by

$$I_0 = k_1, \quad (15)$$

$$I = k_2 C_F^{\ddagger}. \quad (16)$$

Substituting $C_F^{\ddagger}$ from Eq. (14), we have

$$\left(\frac{I_0}{I} - 1\right) \Big/ C_Q = \left(\frac{k_1}{k_2 C_F^{\ddagger}} - 1\right) \Big/ C_Q = \frac{k_3}{k_2} = k_Q.$$
$$(17)$$

To obtain k_3 the true rate constant of the quenching reaction from k_Q, it is necessary to multiply by k_2. This is equivalent to dividing by the mean life of fluorescence, a quantity which may be determined for any particular fluorescent substance by direct optical measurement,[36] or indirectly by studying the effect of viscosity on the polarization of the fluorescent emission.[37, 38] Since quenching has an activation energy of about 4 kcal., i.e., similar to that of diffusion, a linear relation between k_Q and diffusion (fluidity) has been postulated by many authors,[32, 38, 39] but experimental curves show deviations from linearity (see Fig. 4.1) which have not received satisfactory explanation.

When the reactants are ions, the almost obvious dependence upon ionic strength has been observed.[40, 41] There is also a self-potential effect. In this connection it should be pointed out that any attempt[40] to base a decision of the mechanism between the concept of "an ordinary bimolecular reaction between the quenching ion and the activated dye molecule" and that of "de-activation of the photo-activated molecule by collision with the quenching ion in which some energy is transferred to the quencher" by testing the agreement with the Brönsted activity coefficient factor is doomed to failure. The number of effective collisions is *not* determined by the activities of the colliding molecules *alone*. Brönsted's equation can be justified equally well from an equilibrium viewpoint as from a purely collisional or diffusional viewpoint. (Reference 3, p. 2668.)

Since most investigators of fluorescence quenching have been unaware of the importance of these electrostatic complications, there are few data in the literature that can be interpreted unambiguously. It is evident, however, that the plot of k_Q vs. fluidity ($1/\eta$) is never linear, whether the viscosity (η) is varied by changing the medium, or by varying the temperature. Figures 4 to 7 demonstrate that when the medium is varied at constant T, use of the normalized mole fraction

[33] Weiss, Trans. Faraday Soc. **35**, 48 (1939).
[34] Bowen, Trans. Faraday Soc. **35**, 15 (1939).
[35] Rollefson and Stoughton, J. Am. Chem. Soc. **63**, 1517 (1941).

[36] Gaviola, Zeits. f. Physik **42**, 853, 862 (1927); Szymanowski, *ibid*. **95**, 440 (1935).
[37] F. Perrin, Thesis, Paris, France (1929).
[38] Wawilow, Acta. Physicochim. U.S.S.R. **7**, 49 (1937).
[39] Svešnikov, Acta Physicochim. U.S.S.R. **7**, 755 (1937).
[40] Stoughton and Rollefson, J. Am. Chem. Soc. **61**, 2634 (1939).
[41] Stoughton and Rollefson, J. Am. Chem. Soc. **62**, 2264 (1940).

constant k_Q^N reduces the curvature considerably.*

The quenching of fluorescein[39] (Fig. 7) and of rhodamine-B[32] (Fig. 6) by potassium iodide are ionic reactions. The most interesting result in the latter case is that obtained when pure methanol is the solvent. In this case k_Q is found to be much greater than in water, although iodide ion is known to diffuse more slowly in methanol. After normalization the ratio of k_Q in water and in methanol is 1.40, while the ratio of the mobilities of iodide ion is 1.25 and of the diffusion constants of potassium iodide is 1.26.

The quenching of acridone by potassium iodide[41] and the quenching of rhodulin red by aniline[39] involve a neutral molecule and should be much less dependent upon dielectric constant. In both cases the plot of k_Q^N vs. $1/\eta$ is linear. The case of rhodulin red is particularly interesting, since the quencher is the comparatively large and neutral aniline molecule, which might be expected to obey Stokes' law, and since pure alcohols were used as solvents.

It can hardly be a coincidence that the percent deviation from a straight line through the origin of points, obtained in a series of alcohols of molecular weights ranging from 32 to 85, should be closely proportional to the molecular weights. It is to be noted that the anomaly in the order of
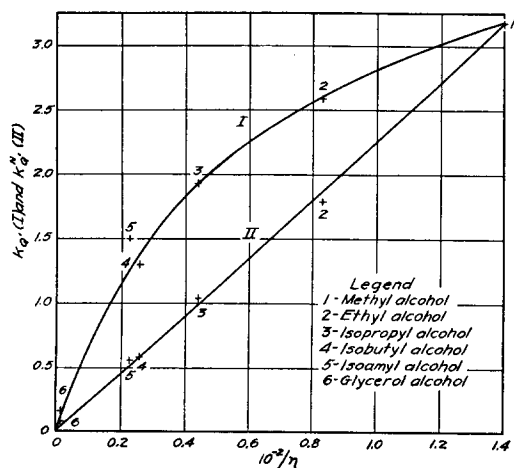

FIG. 5. The quenching of fluorescence of acridone by potassium iodide. Data of Stoughton and Rollefson.

FIG. 4. The quenching of fluorescence of rhodulin red by aniline. Data of Svešnikov.

*The symbol k_Q or k_Q^N, used in the figures, denotes the first-order constant $(I_0/I - 1)$ obtained with C_Q held constant.
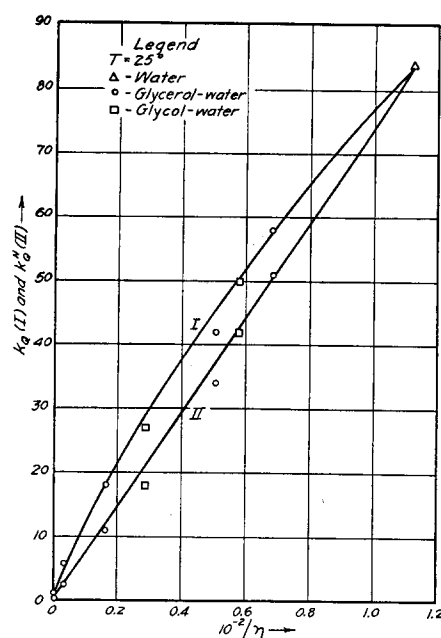
the points obtained in isobutyl and isoamyl alcohols is removed by normalization to the mole fraction scale.

The significance of this linear plot is not entirely clear, and cannot be explained, at least until a thorough experimental analysis of the problem, involving a determination of diffusion coefficients, has been made. It must be emphasized that a mere change of scale cannot reduce the curvature of the plot of k vs. $1/\eta$ when the latter is varied by changing the temperature and holding the solvent composition constant; and in the case of the quenching of rhodulin red by aniline, certain points obtained in glycerol-ethanol mixtures fall on a smooth curve with the points obtained in pure solvents before normalization to a mole fraction scale, but apparently do not fall on the linear plot after normalization.

Nevertheless the quenching of fluorescence is an example of a type of reaction in the study of which the concentration scale is very important and for which we find use of the mole fraction scale gives a simple result. Quenching involves a diffusion process as a rate determining step. Experiments are in progress to determine, if possible, whether the cage model Eq. (10) or the Smoluchowski type equations fit the data best.

D. Other Solvent Effects. The Solubility of Thallous Chloride

The rate of isomerization of ammonium cyanate[15,42] and of the carbinol formation of bromphenol blue[14,15] is slower in glycol-water mixtures than in the isodielectric methanol-water solutions. In such a case it is evident that use of k^N will make the discrepancy worse. The order, by effect on the rate, of the added solvents, methanol, ethanol, glycol, is the order of their increasing molecular weights and viscosities;[15] but whether we reason from an equilibrium rate theory or from Eq. (9) we must conclude that viscosity cannot directly affect the rate, since large energies of activation are involved.

If the equilibrium theory of reaction rate is correct, solvent effects should not be peculiar to ionic kinetics, but should be found for ionic equilibria in general. We have, therefore, measured the solubility of thallous chloride in several isodielectric solvents (Table IV). While no such extended analysis as that given by Hogge and Garrett[13] for ethanol-water mixtures has been attempted, it is possible to draw certain conclusions:

The solubility cannot be predicted unambiguously from the dielectric constant. It depends upon the solvent added to water and increases in the order of added solvents methanol, ethanol, t-butanol, glycol, mannitol. This is consistent with a *decrease* in reaction rates, which involve the factor $f_A f_B / f_X$. A general decrease in the activity coefficients, corresponding to a proportional increase in the solubility of reactants *and critical complex*, would decrease the reaction rate. The solubility of thallous chloride in water is actually increased by adding mannitol. Dielectric constant effects are here of less importance than another effect, apparently related to the size of the mannitol molecule. The addition of glycine increases the solubility, but less than would be predicted from the ethanol-water data.

CONCLUSIONS

One conclusion may be drawn; namely, that use of the mole fraction scale instead of the volume molar scale leads to distinctly simpler

and more consistent results in various solvents in the specific case of the bromacetate-thiosulfate reaction.

The more general conclusion, that the mole fraction scale should always be used in comparing rate constants in different solvents, is in a sense an academic one requiring no experimental verification. As Scatchard clearly states[1] the only object is to choose that scale which will allow the specific solvent effects to be most readily accounted for by activity coefficients determined by the physical properties of solute and solvent.

The basis of any mole fraction ideal law of solution is the assumption that the number of available positions in a liquid is proportional to the total number of molecules present and that all positions are equally available for all molecules, regardless of size or shape. Then any size-shape effects must be compensated for by activity coefficients. If there are other deviations from ideality, i.e., if the forces between solvent-solvent, solvent-solute, and solute-solute pairs of molecules are appreciably different, these deviations must also be compensated by an activity coefficient.
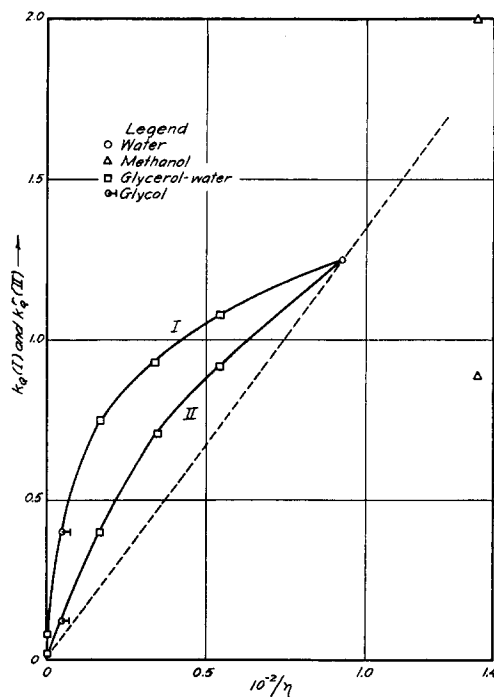

FIG. 6. The quenching of fluorescence of rhodamine B by potassium iodide. Data from Frank and Wawilow.

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[42] Svirbely and Schramm, J. Am. Chem. Soc. **60**, 330 (1938); Lander and Svirbely, *ibid.* **60**, 1613 (1938).
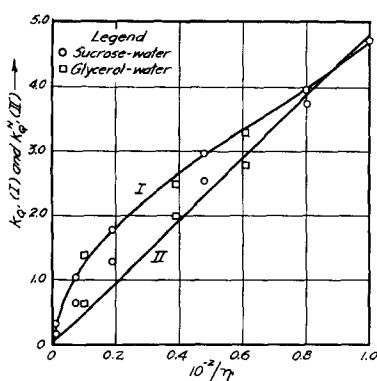
FIG. 7. The quenching of fluorescence of fluorescein by potassium iodide. Data from Svešnikov.

There are no equations available for precise calculation of non-electrostatic activity coefficients. The approximate equation valid, for "regular" solutions[27]

$$RT \ln \gamma_1 = v_1 \left(\frac{N_2 v_2}{N_1 v_1 + N_2 v_2} \right)^2 \times \left[\left(\frac{E_{11}}{v_1} \right)^{\frac{1}{2}} - \left(\frac{E_{22}}{v_2} \right)^{\frac{1}{2}} \right]^2, \quad (18)$$

where the subscripts 1 and 2 refer to solute and solvent, respectively, N = mole fraction, v = molar volume, and E's are potential energy terms that may be replaced by the energies of vaporization of the pure liquids, predicts a relationship between solvent effects and the ratio E_{22}/v_2. This however does not vary significantly in the aqueous mixtures discussed in this paper.

Except in certain special cases the effect of differences in size of solvent and solute molecules cannot be neglected. In the case of approximately rod-shaped molecules it has been shown theoretically and experimentally[43,44] to be zero: Thus, n-hexane and n-hexadecane obey the mole fraction ideal laws throughout the entire range of concentration. For other shapes, it has been sug-

gested[45,46] that there may be large deviations from the mole fraction laws and that these deviations are an increasing function of the ratio of the molar volumes of solute and solvent. For spherical molecules A and B with $v_A = 1/2v_B$, the equations of Chang lead to a value of about 0.8 for the activity coefficient of the very dilute solute, A.[47]

The simplicity of the results found for the bromacetate-thiosulfate reaction must be due to a considerable cancellation of the non-electrostatic activity coefficients of the reactants with those of the critical complex. No such cancellation is likely in the case of solubility or for a reaction such as the carbinol formation of brom-phenol blue[14] in which the critical complex closely resembles one of the reactants.

SUMMARY

New data are presented to emphasize the difficulties of comparing reaction rate constants obtained in different solvents. It is shown that use of a mole fraction concentration scale instead of the usual volume molar scale gives a simpler result for the kinetics of the bromacetate-thiosulfate reaction.

Temperature coefficients have been determined for this reaction and are discussed as criteria of electrostatic and non-electrostatic effects.

It is suggested that determination of the energy and entropy of activation with the product DT and the concentration of reactants held constant helps in interpreting the kinetics of ionic reactions.

Data on the solubility of thallous chloride in solvents of different molecular volume are presented to show that there are other specific solvent effects as important as the electrostatic effects.

Examples of the effect of choice of concentration scale upon the interpretation of data are taken from the literature. The quenching of fluorescence in solution as determined by the viscosity is discussed.

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