

[CONTRIBUTION FROM THE CHARLES EDWARD COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY]

Dielectric and Solvent Effects upon the Alkaline Fading of Brom Phenol Blue

BY EDWARD S. AMIS AND SHIRL E. COOK

One noticeable effect of the solvent in kinetic measurements is the influence upon the frequency factor B in the Arrhenius equation due to electrostatic phenomena arising from the dielectric constant of the medium and to specific solvent effects which are characteristic of the solvent for a given reaction. Warner¹ and his co-workers² working with the reaction between the ammonium and cyanate ions in methyl alcohol-water solvent observed the constancy of the Arrhenius B term in isodielectric media and the marked difference of B measured in iso-composition and isodielectric media. A like difference of the energy of activation was also theoretically explained by them for media of zero ionic strength. Lander and Svirbely³ using the same reaction in glycol-water media observed similar phenomena for iso-composition and isodielectric solvents. LaMer and his co-workers⁴ investigating the reaction between the negative divalent brom phenol blue ion and the negative univalent hydroxide ion in methyl alcohol-water and ethyl alcohol-water solvents obtained similar results. The mechanism they proposed for the reaction was $B \cdot \phi B^{-2} + OH^{-} \rightleftharpoons$ colorless carbinol. They emphasized the entropies of activation in media of constant composition and media of constant dielectric constant. LaMer⁵ has derived an equation showing that, when the dielectric constant of the media does not vary, the part of the entropy of activation arising from electrostatic forces between charged reactants is zero. This is an explanation for the constancy of B in iso-dielectric media, since the change of B with composition of solvent is largely due to the temperature coefficient of the dielectric constant of the solvent.

An equation has been derived by Amis and Holmes⁶ from which the difference in energies of activation in dilute solutions between constant composition and constant dielectric constant media can be calculated. If we consider the general kinetic equation^{7,8,9,10} which in the case of

very dilute solutions can be written

$$\ln k = \ln k_{\infty} - \frac{Z_A Z_B N e^2}{DRT r} + \frac{Z_A Z_B N e^2}{DRT} \kappa \quad (1)$$

we can, by multiplying both sides of the equation by T , differentiating with respect to T , considering T and D as variables, then differentiating with respect to T , holding D constant and subtracting the latter expression from the former, obtain an equation for the difference of the Arrhenius frequency factor B , when comparing kinetic measurements in constant composition and constant dielectric constant media. The equation is

$$B_C - B_D = \frac{Z_A Z_B N e^2}{2.3 D^2 R} \left[\frac{1}{r} - \frac{3e}{10} \sqrt{\frac{2\pi N^2 \mu}{10 D R T}} \right] \frac{dD}{dT} \quad (2)$$

In these equations the terms have their usual significance. In deriving this equation it has been assumed that $(T \ln k_{\infty})$ is independent of D .⁶ This equation predicts that for a reaction between an ion and an uncharged molecule the B terms would be the same for both kinds of media. This is not true, for ion-dipole forces may cause slight differences of B in the two types of solvents. Since dD/dT is negative for ordinary solvents, equation (2) further predicts that for ions of like sign the Arrhenius B observed in constant composition media is less than the same quantity measured in iso-dielectric solvents and vice versa for ions of unlike sign. Specific solvent effects have been noted by many investigators^{3,6} in the field of solution kinetics. For the fading reaction of brom phenol blue and sodium hydroxide Amis and LaMer¹¹ noted only slight solvent effects when comparing methyl alcohol-water and ethyl alcohol-water media. An additional investigation of this problem was undertaken to examine further the effects of solvents upon reaction rates and to obtain data from which it was hoped that added support might be given equation (2).

Experimental

The brom phenol blue in this investigation was Eastman (E. K. C.) no. 752 tetrabromphenolsulfonphthalein of the same quality used by Amis and LaMer in their investigation of the fading reaction and a stock solution (2×10^{-4} molar) of dye was prepared in an identical way. Fresh stock solutions were made up at intervals, so that in no case was the solution used in a kinetic run over six weeks old.

- (1) Svirbely and Warner, *THIS JOURNAL*, **57**, 1883 (1935).
- (2) Svirbely and Schramm, *ibid.*, **60**, 330 (1938).
- (3) Lander and Svirbely, *ibid.*, **60**, 1613 (1938).
- (4) LaMer and Amis, *ibid.*, **61**, 905 (1939).
- (5) LaMer, *J. Franklin Inst.*, **225**, 709 (1938).
- (6) Amis and Holmes, *THIS JOURNAL*, **63**, 2231 (1941).
- (7) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 137 (1925).
- (8) Christiansen, *ibid.*, **113**, 35 (1924).
- (9) Scatchard, *THIS JOURNAL*, **62**, 52 (1930).
- (10) Scatchard, *Chem. Rev.*, **10**, 229 (1932).

(11) Amis and LaMer, *THIS JOURNAL*, **61**, 905-912 (1939).

TABLE I
 DATA FOR WATER AND GLYCEROL-WATER MEDIA

Temp., °C. ^a	Constant composition, variable dielectric					
	H ₂ O		40% glycerol		60% glycerol	
	<i>k</i>	<i>D</i>	<i>k</i>	<i>D</i>	<i>k</i>	<i>D</i>
10°	20.2	84.26	6.07	72.23	3.09	64.8
35°	129.0	74.88	36.2	63.86	19.2	57.0
60°	621.0	66.63	175	56.24	96.4	50.2
<i>B</i> ₁₀₋₃₅ °	11.20		10.37		10.20	
<i>B</i> ₃₅₋₆₀ °	11.20		10.69		10.60	
Δ <i>E</i> * ₁₀₋₃₅ °	12,840		12,360		12,630	
Δ <i>E</i> * ₃₅₋₆₀ °	12,760		12,800		13,120	

Temp., °C. ^a	Isodielectric, variable composition							
	<i>D</i> = 60.0		<i>D</i> = 64.8		<i>D</i> = 68.6		<i>D</i> = 72.2	
	<i>k</i>	Wt. % glycerol	<i>k</i>	Wt. % glycerol	<i>k</i>	Wt. % glycerol	<i>k</i>	Wt. % glycerol
10°	3.09	60.0	3.62	55.7	6.06	40.0
35°	21.4	52.3	41.6	37.0	49.6	30.2	92.0	9.9
60°	256	26.0	500	7.5	621	0.0
<i>B</i> ₁₀₋₃₅ °	...		15.25		15.45		15.40	
<i>B</i> ₃₅₋₆₀ °	15.70		15.09		16.35		...	
Δ <i>E</i> * ₁₀₋₃₅ °		18,000		18,100		18,820	
Δ <i>E</i> * ₃₅₋₆₀ °	20,180		20,210		20,570		

^a The *B* values are in days⁻¹.

The sodium hydroxide was Baker and Adamson reagent grade. A solution was made up and standardized according to the procedure of Amis and LaMer.

The glycerol was Merck reagent glycerin. This was purified by distillation according to the method used by Akerlof.¹² The first one-third of the distillate was rejected and after collecting a volume equal to about one-half of the original volume in the still, the remainder was discarded.

All volumetric apparatus and weights were calibrated.

The thermostats were constant to within ±0.05° at 10 and 60° and to within ±0.005° at 35° and were standardized against B. S. thermometers.

The experiments were performed by weighing out the glycerol, adding the dye solution followed by the alkali and adjusting the final volume to make the dye 2 × 10⁻³ molar and the sodium hydroxide 0.09 molar. The instrument used for analysis was a Klett colorimeter. The colorimetric standards were made up freshly from stock solutions of alkali and dye each time a reading was taken. Any perceptible fading of the unknown during the period of observation should be compensated by fading of the standard.

An average of five settings of the instrument was taken for the value used in the calculations. A Mazda lamp with a blue filter furnished illumination and the instrument was shielded from outside light by means of a black cloth-enclosed compartment.

The dielectric constants of the solvent mixtures were taken from Akerlof.¹²

Discussion of Data

In Table I are recorded values of *k* for the reaction between negative divalent brom phenol blue ion and univalent hydroxide ion in iso-composition and iso-dielectric glycerol-water solvent.

(12) Akerlof, THIS JOURNAL, 54, 4125-39 (1932).

The *k* values were calculated as pseudounimolecular rate constants in days according to the equation

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad (3)$$

and converted to the bimolecular rate constant in moles per liter per day by dividing by the concentration of alkali. Each value of *k* recorded in the table is the mean of at least two duplicate runs, from five to eight separate observations being made for each run. The variation from the mean of the duplicate runs was always in the last significant figure; many duplicates gave exactly the same average value of *k*. This table also includes the energies of activation and the frequency factor *B* in the Arrhenius equation calculated from these rate constants. The frequency factor is in days⁻¹.

In constant dielectric constant media Δ*E** has a pronounced temperature coefficient, becoming larger at higher temperature ranges. In iso-composition media no definite trend in the energies of activation is noticeable.

In Fig. 1, log *k* vs. 1/*D* is plotted for glycerol-water solvent. Straight lines down to a dielectric of 55 (1/*D* = 1.8 × 10⁻³) are obtained. This agrees with the observations of LaMer and his co-workers.^{5,11}

From Table I it is observable that the energies of activation for different constant-dielectric constants of glycerol-water media are opposite in

TABLE II

A COMPARISON OF $B_C - B_D$ CALCULATED FROM EQUATION (2) AND THE OBSERVED VALUES FOUND IN THE LITERATURE

Observer	Reaction	Solvent	$\sqrt{\mu}$	r in Eq. (2), A.	Inter-med. dielec. (for const. comp.)	Dielec. range (iso-dielectric)	$B_C - B_D$ calcd.	$B_C - B_D$ obs.
This paper	$B. \phi B.^- + OH^-$	Glycerol-water	0.300	1.75	74.9	72.2-60.0	-3.86	-4.17
			.300	1.75	63.9	72.2-60.0	-4.57	-4.45
			.300	1.75	57.0	72.2-60.0	-5.14	-4.97
Amis and Holmes	Sucrose + H_2O^+	Dioxane- H_2O	.316	60.0-45.0	0.00	0.60
		EtOH- H_2O	.316	68.2-45.0	0.00	-0.34
Amis and LaMer	$B. \phi B.^- + OH^-$	MeOH- H_2O	.300	1.30	78.54	71.42-64.86	-5.40	-5.75
			.300	1.30	71.42	71.42-64.86	-6.00	-6.34
			.300	1.30	64.55	71.42-64.86	-6.41	-5.90
		EtOH- H_2O	.1415	1.30	78.54	71.42-64.86	-6.08	-5.79
			.300	1.20	78.54	71.42-64.86	-5.95	-5.96
			.300	1.20	71.42	71.42-64.86	-6.75	-7.19
			.300	1.20	64.55	71.42-64.86	-7.10	-7.23
.1415	1.20	78.54	71.42-64.86	-6.49	-5.99			
Svirbely and Warner	$NH_4 + CNO^-$	MeOH- H_2O	.194	2.00	69.8	63.5	1.96	2.44
			.194	2.00	69.8	55.0	1.96	2.65
			.000	2.00	69.8	63.5-55.0	2.43	2.98
Svirbely and Schramm			.194	2.00	63.5	63.5-35.0	2.25	2.16
			.194	2.00	69.8	63.5-35.0	1.96	2.59
			.000	2.00	63.5	63.5-35.0	2.84	2.57
			.000	2.00	69.8	63.5-35.0	2.43	3.02
Lander and Svirbely		Glycol-	.194	2.50	69.76	63.5-40.0	1.47	1.57
			.000	2.50	69.76	63.5-40.0	1.95	2.34

trend to the theory proposed by Amis¹³ and hence cannot be accounted for on the basis of electrostatics.

This opposite trend can be explained by the formation of a compound between sodium hydroxide and glycerol, stable at higher concentrations of glycerol, but progressively more hydrolyzed at higher temperatures and below certain concentration values. This viewpoint is supported by the statement of Lippman¹⁴ that the alkali compounds of glycerol are dissociated by strong dilution of their solutions. In support of this supposition the authors have plotted (Fig. 2) the reaction rate constant corrected for dielectric effects against the mole fraction, N_2 , of glycerol at various temperatures. It can be observed from this plot that the change in slope of the curve in approaching the water point becomes more marked at higher temperatures, as would be the case with decreased stability of the alkali-glycerol compound and the consequent freeing of the bound hydroxide ion. Also at higher concentrations of glycerol, k is directly proportional to the mole fraction of this substance, as is shown by the

flattening out of the curves for larger values of N_2 . That the curves actually approach a straight

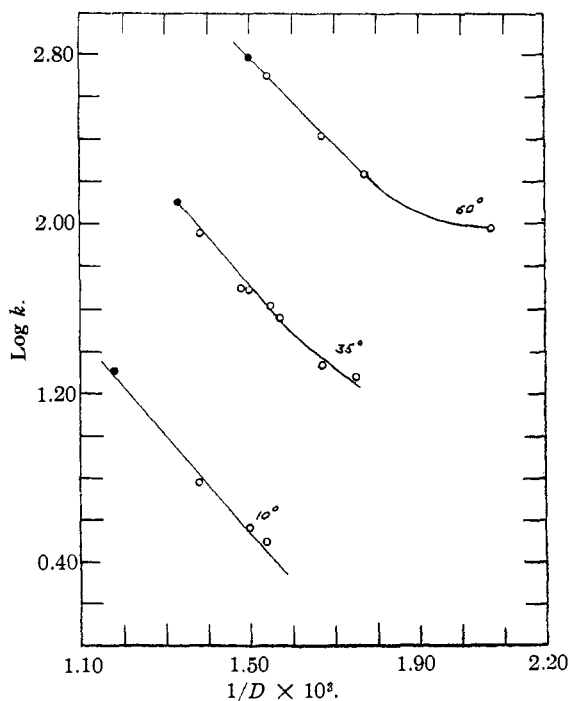


Fig. 1.—Log k as a function of $1/D$: ●, water; ○, glycerol-water.

(13) Amis, paper in THIS JOURNAL, 63, 1606 (1941).
 (14) Lippman, "Die Chemie der Zuckerarten," third edition revised, F. Vieweg and Son, Braunschweig, 1904, p. 1322.

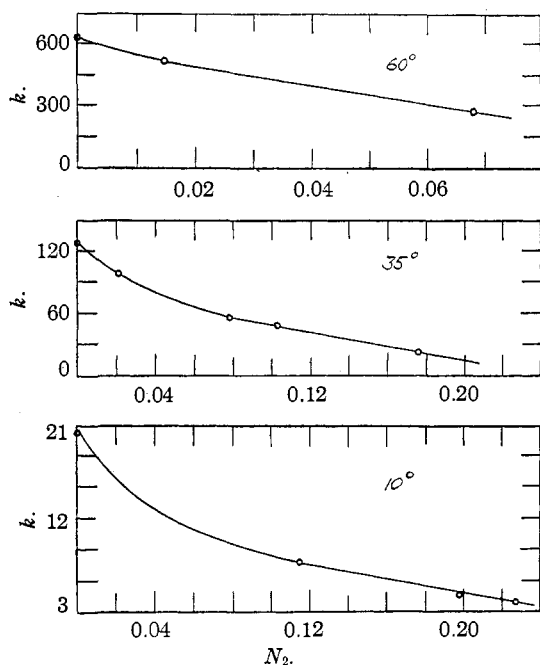
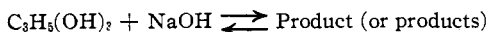


Fig. 2.—Bimolecular velocity constant in days as a function of the mole fraction of glycerol.

line in this region of concentration is quite evident from the plots, and shows that the mass action law applied to the equation



is holding.

Although the scales used in Fig. 2 are such as to obscure the relative slopes of the three curves, there is a progressive increase of slope with increasing temperature: thus it can be seen that k increases relatively faster with decrease of mole fraction of glycerol at higher temperatures than at lower temperatures. This effect predominates over the electrostatic effect and gives an opposite trend to the energies of activation from that which electrostatics would predict. In a similar manner Amis and Holmes⁶ explained the data for the acid inversion of sucrose in ethyl alcohol-water media.

In Table II is given a comparison of the difference of $B_C - B_D$ calculated from equation (2) and the observed quantity from this investigation and other investigations found in the literature. The dielectric used in these calculations was the dielectric of the constant composition run for the mid-point of the temperature range. No electrostatic corrections were necessary to bring the constant dielectric runs to the same dielectric as the constant composition run, since the value of B is sensibly constant for all values of D when meas-

urements are made at constant dielectric constant. The value for B_D was obtained by averaging all the B terms given at constant dielectric constant. The B_C used was the average for the temperature range at a given composition. The magnitude and sign of the observed and calculated values are in good agreement in all cases, even though the values of r used for calculating $B_C - B_D$ were not always those which could have been chosen for closest agreement between experimental and calculated data but were the values of r used in the equation for calculating $\Delta E_C^* - \Delta E_D^*$ in the paper of Amis and Holmes.⁶ Always the same value of r can be used at different dielectrics for the same solvent pair. However, different solvent pairs for the same reaction require slightly different values of the parameter. For example: the value of r for the brom phenol blue fading reaction is 1.20, 1.30, and 1.75 for ethyl alcohol-water, methyl alcohol-water, and glycerol-water, respectively. This is in agreement with the observations of Amis and LaMer¹⁵ and Amis and Holmes⁶ for this reaction. Likewise a difference for r values is noted for the ammonium ion-cyanate ion reaction in methyl alcohol-water and glycol-water solvents, being greater for the glycol-water solvents. This is supported by the findings of Amis¹³ and Amis and Holmes.⁶

Summary

The reaction between the negative divalent brom phenol blue ion and the negative univalent hydroxide ion was studied in iso-composition and iso-dielectric glycerol-water media over the temperature range 10–60°.

The energies of activation measured in glycerol-water media were opposite in trend to the predictions of electrostatic theory and were attributed to an equilibrated reaction between sodium hydroxide and glycerol. The measured rates corrected for dielectric effects were proportional to the mole fraction of glycerol at the higher concentrations of this component of the binary solvent. At lower concentrations of glycerol, however, k is no longer proportional to the mole fraction of this substance and rapidly approaches the water point. This sharp break in the trend was attributed to the hydrolysis of the compound formed between glycerol and sodium hydroxide at lower concentrations of glycerol. This theory is supported by the shape of the k vs.

(15) Amis and LaMer, *This Journal*, **61**, 905-912 (1939).

mole fraction curves at different temperatures.

An equation was derived for calculating B_C — B_D and was shown to be in agreement with the re-

sults of this investigation and with data recorded in the literature.

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Contributions to the Chemistry of Indium. III. An Electrometric Study of the Precipitation of Hydrous Indium Hydroxide¹

BY THERALD MOELLER

Attention already has been directed to the fact that, while the term "neutral" as applied to aqueous indium salt solutions often appears in the literature, such usage is incorrect because any attempt to bring a solution containing indium ion to the neutral point will result in precipitation of the hydrous hydroxide.²

Inasmuch as reported quantitative investigations of the changes in *pH* during the addition of bases to indium salt solutions appear to be limited to a single titration of an indium nitrate solution with sodium hydroxide,³ it was deemed advisable to make more extensive observations of this nature with the ultimate aim of estimating the solubility and solubility product of indium hydroxide.

Furthermore, since the solubility of hydrous indium hydroxide in concentrated sodium and potassium hydroxide solutions has been thought of as involving indiate formation,⁴ it was hoped that data from such titrations might either support or refute this contention.

Experimental

Materials Used.—Pure anhydrous indium sulfate was prepared from indium metal (stated to be 99.98% pure) as previously indicated.² Anhydrous indium chloride was obtained by chlorinating the metal and repeatedly subliming the product in dry nitrogen.⁵ Crystals of the hydrated nitrate, corresponding by analysis to $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$, were prepared by treating the pure oxide with dilute nitric acid in slight excess, evaporating to crystallization on the steam-bath, and drying the product over anhydrous calcium chloride for two months. Solutions obtained by dissolving these salts in distilled water and standardized by gravimetric determination of the indium as oxide² were of the following concentrations: $\text{In}_2(\text{SO}_4)_3$, 0.0493 *M*; $\text{In}(\text{NO}_3)_3$, 0.1000 *M*; InCl_3 , 0.1000 *M*.

Tenth-normal solutions of sodium, potassium and am-

monium hydroxides were obtained by diluting concentrated, carbonate-free solutions with carbon dioxide-free water. The sodium and potassium hydroxide solutions were standardized against primary standard potassium acid phthalate, using phenolphthalein as indicator, while the ammonium hydroxide was standardized against 0.1 *N* hydrochloric acid (using methyl red) which had previously been standardized against sodium hydroxide. All bases were protected against carbon dioxide with soda lime.

Experimental Procedure.—A 10-ml. portion of the indium salt solution was diluted to 40 ml. and placed in a thermostat controlled to $\pm 0.5^\circ$ of the desired temperature. While the solution was vigorously stirred, the base was added in small increments, the changes in *pH* being followed with a Beckman laboratory model G *pH* meter, the glass electrode of which had been calibrated against a standard 0.05 *M* potassium acid phthalate buffer. No attempt was made to protect the titration vessel from the carbon dioxide of the air because the only changes in *pH* due to carbonate formation were in regions of high *pH* where the alkali ion error becomes appreciable. In all instances, except where the *pH* changed markedly with small increases in added hydroxyl ion, equilibrium was attained rapidly.

Titrations were made at 40, 25 and 10°, and the effects of initial indium ion concentration were studied at 25°.

Results and Discussion

Studies at 25°.—Plotted in Fig. 1 as *pH vs.* the mole ratio of hydroxyl ion added to indium ion initially present are data obtained from titrations of indium nitrate, chloride and sulfate solutions with sodium, potassium and ammonium hydroxides. For each curve, the point (av.) at which precipitation began and the point (av.) at which flocculation of the colloidal suspension produced by the addition of the base occurred are indicated, respectively, by singly and doubly barbed arrows. For each indium salt agreement among the data for the three bases is excellent, particularly in the precipitation region bounded by the arrows.

Although with both the nitrate and sulfate solutions precipitates appeared only after the ratio of OH^- to In^{+++} reached 0.84, whereas with

(1) Presented before the Division of Physical and Inorganic Chemistry on April 8, 1941, at the 101st meeting of the American Chemical Society at St. Louis, Missouri.

(2) Moeller, *THIS JOURNAL*, **62**, 2444 (1940).

(3) Oka, *J. Chem. Soc. Japan*, **59**, 971 (1938).

(4) Renz, *Ber.*, **34**, 2763 (1901).

(5) Moeller, *THIS JOURNAL*, **63**, 1206 (1941).