

[CONTRIBUTION NO. 837 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

## The Viscosities of Aqueous Solutions of Amino Acids at 25 and 35°

BY L. S. MASON, P. M. KAMPMAYER<sup>1</sup> AND A. L. ROBINSON

The viscosities of aqueous solutions of five amino acids have been measured at 25 and 35° at a series of concentrations. The relative viscosities of these solutions have been expressed as a function of concentration; the function is non-linear in all cases. The activation energy for viscous flow,  $E^*$ , and the quantity  $\Delta E^* = E_{\text{H}_2\text{O}}^* - E_{\text{soln}}^*$ , the differential activation energy, has been calculated for solutions of these amino acids. A general correlation between  $\Delta E^*$  (calculated from viscosities at 25 and 35°) and  $S_1 - S_1^0$  (calculated from heats of dilution at 25°) has been demonstrated.

## I. Introduction

The viscosities of solutions of electrolytes have been studied carefully, and interpreted in terms of the Debye-Hückel theory.<sup>2,3</sup>

A satisfactory theory for zwitterions, comparable to the Debye-Hückel theory for electrolytes, has not yet been formulated<sup>4-6</sup> although a theoretical derivation has shown a linear relationship between partial molal quantities and concentration in the limit of dilute solutions. Experimental confirmation of the latter relationship exists in the case of glycine, and  $\alpha$ - and  $\beta$ -alanine and other amino acids.<sup>7-10</sup> Studies of the heats of dilution of aqueous solutions of amino acids<sup>7,8,11,12</sup> have made possible the calculation of differential entropies of dilution.<sup>12,13</sup> Robinson<sup>13</sup> has related these differential entropies of dilution to structure strengthening and structure weakening effects of the solute upon the quasi-solid structure of water and, calling attention to the fact that the meager viscosity data available for amino acid solutions were in qualitative agreement with this concept, suggested that more extensive data would be of interest for a further discussion of the effects of amino acids on the structure of water. Part of the work reported here stems from this suggestion.

Of the ten amino acids for which heats of dilution have been measured and differential entropies calculated,<sup>14</sup> five (glycine,  $\alpha$ - and  $\beta$ -alanine,  $\alpha$ -amino-*i*-butyric acid, and  $\alpha$ -amino-*n*-valeric acid) were chosen for the present study. The selection of these five amino acids was made because they represent the extremities and the center portion of the fan-like family of curves obtained by plotting the relative apparent molal heat content or the differential entropy of dilution *versus* concentration

( $\alpha$ -amino-*n*-valeric acid was chosen rather than  $\epsilon$ -aminocaproic acid due to its greater solubility and lower cost).

## II. Experimental

(1) **Apparatus and Procedure.**—Two viscometers of the modified Ostwald type were constructed from Pyrex glass. The effective volume of flow for both viscometers was ca. 28 ml. The capillary path length was approximately 35 cm.; the radius of the capillary bore was 1 mm. for ca. two-thirds of the path length and 2 mm. for the remainder in the case of viscometer No. 1; the radius of the capillary bore for viscometer No. 2 was 1 mm. for the entire path length.

Both viscometers were attached permanently to brass plates by soldered copper strips and deKhotinsky cement, the brass plates constituting part of the kinematic mountings for the viscometers. The other parts of the kinematic mountings were attached to a length of 1" angle iron suspended rigidly over two adjacent water-baths so that each viscometer, in turn, could be placed in either water-bath.

For precise work, and especially for viscometers other than those of elaborate design constructed by expert glass blowers, Poiseuille's original equation needs modification to take into account a kinetic energy term. The exact form of this kinetic energy term has been the subject of some controversy.<sup>15-20</sup> For a given constant volume of flow Poiseuille's equation, including the kinetic energy correction term, can be expressed by the equation

$$\eta = cdt - Kd/t \quad (1)$$

where  $d$  = density,  $t$  = efflux time, and  $c$  and  $K$  are constants characteristic of the viscometer in question for a constant charge of liquid and may be evaluated, given the efflux times, densities and viscosities of a liquid at two different temperatures.

The constant charge of liquid to each viscometer was 50.0 ml. The absolute viscosities of water were taken as 8.9027 and 7.1903 millipoises at 25 and 35°, respectively; the selection of these values is discussed elsewhere.<sup>21</sup> The calculated values for the constants,  $c$  and  $K$ , in equation 1 are given in Table I. In this table,  $n$  refers to the number of determinations of efflux time, the data being collected over a period of several months. The precision indicated is a standard error of the mean defined here as

$$\text{S.E.M.} = \sqrt{\frac{\sum(X - \bar{X})^2}{n(n-1)}}$$

where  $X$  is the observed quantity and  $\bar{X}$  is the mean of  $n$  values of  $X$ .

Timing was done with a laboratory electric stop-clock reading to 0.2 second but permitting estimation to 0.1 second.

Bath temperatures were maintained constant to within a few thousandths of a degree as checked repeatedly with Beckmann thermometers mounted in the baths and pre-

(1) P. M. Kampmeyer, Ph.D., June, 1951, University of Pittsburgh; Film Research and Development Division, Olin Industries, New Haven, Conn.

(2) G. Jones, *et al.*, THIS JOURNAL, **51**, 2950 (1929), *et seq.*

(3) (a) H. Falkenhagen and M. Dole, *Physik. Z.*, **30**, 611 (1929);

(b) H. Falkenhagen and E. L. Vernon, *ibid.*, **33**, 140 (1932).

(4) G. Scatchard and J. G. Kirkwood, *ibid.*, **33**, 297 (1932).

(5) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

(6) R. M. Fuoss, THIS JOURNAL, **58**, 982 (1936).

(7) W. E. Wallace, W. F. Offutt and A. L. Robinson, *ibid.*, **65**, 347 (1943).

(8) H. A. Benesi, L. S. Mason and A. L. Robinson, *ibid.*, **68**, 1755 (1946).

(9) F. T. Gucker, Jr., I. M. Klotz and T. W. Allen, *Chem. Revs.*, **30**, 181 (1942).

(10) F. T. Gucker, Jr., H. B. Pickard and W. L. Ford, THIS JOURNAL, **62**, 2698 (1940).

(11) L. S. Mason and A. L. Robinson, *ibid.*, **69**, 889 (1947).

(12) L. S. Mason, W. F. Offutt and A. L. Robinson, *ibid.*, **71**, 1463 (1949).

(13) A. L. Robinson, *J. Chem. Phys.*, **14**, 588 (1946).

(14) Glycine,  $\alpha$ - and  $\beta$ -alanine,  $\alpha$ -amino-*n*-butyric acid,  $\beta$ -amino-*n*-butyric acid,  $\alpha$ -amino-*i*-butyric acid,  $\gamma$ -aminobutyric acid, valine,  $\alpha$ -amino-*n*-valeric acid and  $\epsilon$ -aminocaproic acid.

(15) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922, p. 28.

(16) N. E. Dorsey, *Phys. Rev.*, **28**, 833 (1926).

(17) W. Riemann, III, THIS JOURNAL, **50**, 46 (1928).

(18) G. Barr, "A Monograph of Viscometry," Oxford University Press, London, 1931, Chap. II.

(19) E. Hatschek, "The Viscosity of Liquids," G. Bell and Sons, Ltd., London, 1928, Chap. II.

(20) H. Tracy Hall and Raymond M. Fuoss, THIS JOURNAL, **73**, 265 (1951).

(21) Paper in preparation.

viously calibrated against a platinum resistance thermometer calibrated at the Bureau of Standards.

Prior to each charging with liquid the viscometers were cleaned with a 50-50 mixture of concentrated sulfuric and nitric acids, thoroughly rinsed with repeated chargings of distilled water, and dried by a stream of filtered dry nitrogen following a rinse with filtered methanol. After charging with a given, freshly filtered solution, the open end of the viscometer leading to the discharge end of the capillary was protected from contamination by dust with a loosely fitting glass cap; to the other end of the viscometer was attached rubber tubing which was connected to the source of filtered dry nitrogen gas used to force the solution up into the arm of the viscometer containing the fiducial timing marks.

Between six and ten consecutive efflux times were recorded for each filling of a viscometer; if the mean deviation from the mean of these readings was as great as 0.1% the run was abandoned, the viscometer recleaned and recharged, and the run repeated.

Solutions which had been charged into the viscometers as described above remained free of turbidity and gave constant efflux times for periods extending to more than two weeks.

TABLE I

VISCOMETER CONSTANTS,  $c$  AND  $K$ , FOR VISCOMETERS NO. 1 AND NO. 2

Vis-cometer	Viscometer constants $c$	$K$	Efflux time for water at 25°	$n$	Efflux time for water at 35°	$n$
1	0.014912	229.99	623.4g + 0.05	44	515.0 + 0.09	24
2	.010059	110.79	899.9 + 0.13	24	734.1 + 0.18	23

(2) **Materials.**—The glycine was Eastman Kodak Co. chemical grade. It was recrystallized three times from water, and dried at 130° prior to use.

The *dl*- $\alpha$ -alanine was obtained from Merck & Co., Inc. It required recrystallization before densities of its aqueous solutions could be obtained which agreed to within 0.02% with those reported by previous workers.

The  $\beta$ -alanine and *dl*- $\alpha$ -amino-*n*-valeric acid were obtained from the Matheson Chemical Company. They dissolved in water to give colorless clear solutions and were used without further purification, but were dried *in vacuo* prior to use.

The *dl*- $\alpha$ -amino-*i*-butyric acid was that on hand from the heats of dilution studies; it was recrystallized three times from aqueous alcohol and dried at 130°, prior to use. (In the heats of dilution studies referred to, it was found that the most sensitive criterion of purity for this compound, as well as for the other amino acids, "was that a sample of acid have essentially a constant solubility when saturated aqueous solutions were formed successively from the residue from each preceding solution."<sup>22</sup> Densities of aqueous solutions of amino acids, as reported by previous workers, were determined using acids whose purity was established by the above criterion.)

Solutions were made up by dissolving weighed amounts of materials in distilled water and making up to definite volumes in volumetric flasks. Densities were determined in standard manner using 20-ml. pycnometers with ground glass stoppers and capillary necks. The densities at 25° for all solutions used agreed to within 0.02% with the values reported by previous workers; this agreement was interpreted as indicating a satisfactory degree of purity for the materials used.

## Results

**Density Data.**—Density data, calculated without buoyancy correction as desired for use in equation 1, agreed to within 0.02% with the density data determined by previous workers.<sup>12,23,24</sup> Density data for  $\alpha$ -amino-*n*-valeric acid agreed to within 0.02% with those reported by Mason, Offutt and Robinson<sup>12</sup> but it was found that a two-constant equation gave a better fit.

(22) L. S. Mason, *THIS JOURNAL*, **69**, 3000 (1947).

(23) F. T. Gucker, Jr., W. L. Ford and C. E. Moser, *J. Phys. Chem.*, **43**, 153 (1939).

(24) F. T. Gucker, Jr., and T. W. Allen, *THIS JOURNAL*, **64**, 191 (1942).

Density data obtained in this work are summarized in Table II. Densities are expressed in terms of molarity at 25° and molality at 35° so that solutions could be prepared volumetrically at 25°, molarity calculated to molality, and the density-molality relationship expressed for the solutions by the equations given.

TABLE II

DENSITIES (WITHOUT BUOYANCY CORRECTIONS) FOR AQUEOUS SOLUTIONS OF AMINO ACIDS; VALUES FOR THE CONSTANTS IN THE EQUATIONS:

$$d^{25} = 0.99707 + aM - bM^2, M = \text{molarity}; d^{35} = 0.99406 + Am - Bm^2, m = \text{molality}$$

Acid	$a$	$A$	$b \times 10^{-4}$	$B \times 10^{-3}$	Valid at least to: $M$	$m$
Glycine	0.031626	0.030786	7.279	1.689	2.1416	2.3772
$\alpha$ -Alanine	.029069	.028472	7.97	2.143	1.4951	1.6512
$\beta$ -Alanine	.030159	.028426	5.920	0.1423	4.4973	6.2524
$\alpha$ -Amino- <i>i</i> -butyric	.025534	.023291	0	0	1.13585	1.2496
$\alpha$ -Amino- <i>n</i> -valeric	.026403	.025732	15.67	3.349	0.50907	0.5356

**Viscosity Data.**—Data for the relative viscosities of aqueous solutions of the five amino acids investigated in this work are summarized in Table III. In this table,  $n$  refers to the number of determinations of viscosity; viscosity was determined with the use of both viscosimeters for at least one concentration, and the number of concentrations investigated was at least five.

TABLE III

RELATIVE VISCOSITIES OF AQUEOUS SOLUTIONS OF AMINO ACIDS; VALUES OF THE CONSTANTS IN THE EQUATION:

$$\eta_r = 1 + Am + Bm^2 + Cm^3$$

Acid	$A$	$B$	$C$	Max. dev., %	$n$	$m$ up to:
	25°					
Glycine	0.14193	0.013048	0	< 0.2	8	2.3772
$\alpha$ -Alanine	.25253	.034879	0	0.2	8	1.6510
$\beta$ -Alanine	.22472	.026298	0.0017030	< .2	9	6.2524
$\alpha$ -Amino- <i>i</i> -butyric	.35685	.0761	0	< .3	7	1.2496
$\alpha$ -Amino- <i>n</i> -valeric	.42948	.07849	0	.1	6	0.5356
	35°					
Glycine	.14470	.012477	0	.2	8	2.3772
$\alpha$ -Alanine	.23633	.034176	0	.2	8	1.6510
$\beta$ -Alanine	.21620	.028682	0.0010294	< .2	9	6.2524
$\alpha$ -Amino- <i>i</i> -butyric	.32277	.0730	0	.2	8	1.2496
$\alpha$ -Amino- <i>n</i> -valeric	.39992	.063976	0	< .1	5	0.5356

Literature data for the viscosities of aqueous solutions of amino acids are meager and extend over limited ranges of concentration. The relative viscosities of 1 molal solutions of glycine and  $\alpha$ -alanine at 18° were reported by Hedestrand<sup>25</sup> as 1.153 and 1.310, respectively. Bell and Madgin<sup>26</sup> reported that the relative viscosity of glycine solutions is a linear function of concentration up to concentrations of about 1 molal, at both 16 and 40° and that the relative viscosity of alanine is a linear function of concentration up to 0.2 molal at 16°; however, their data are not sufficiently precise for this limited range of concentration to show a significant departure from linearity.

(25) G. Hedestrand, *Z. anorg. Chem.*, **124**, 153 (1932).

(26) A. E. Bell and W. M. Madgin, *J. Chem. Soc.*, **74** (1947).

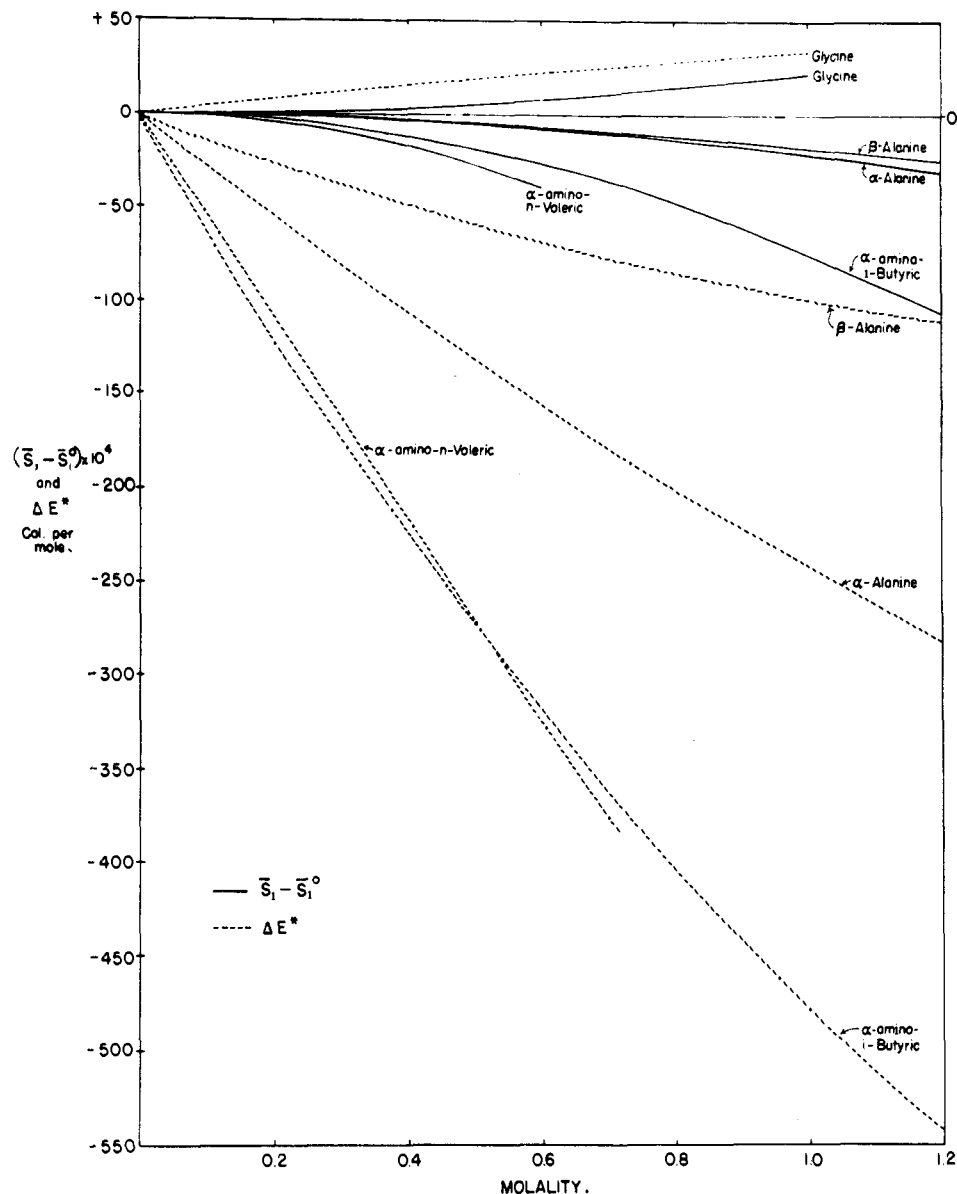


Fig. 1.—Differential entropies of dilution compared with differential activation energies for viscous flow for aqueous solutions of amino acids:  $\bar{S}_1 - \bar{S}_1^0$ —Differential entropies of dilution } cal. per mole.  
 $\Delta E^*$ —Differential activation energies }

Recently, Lyons and Thomas<sup>27</sup> have reported values for the relative viscosities of glycine solutions up to 0.8 molal at 1°. They also derived a linear relationship between relative viscosity and concentration by interpolation of the 16 and 40° measurements of Bell and Madgin.

In view of the paucity of literature data for the viscosities of aqueous solutions of amino acids, it seems appropriate to present here comparisons between data from the literature and the data obtained in this work. These comparisons are presented in Table IV.

III. Discussion

The Arrhenius equation expressing viscosity as a function of temperature may be written as

$$\ln \eta = \alpha + E^*/RT$$

(27) M. S. Lyons and J. V. Thomas, THIS JOURNAL, 72, 4506 (1950).

TABLE IV  
 THE RELATIVE VISCOSITIES OF AQUEOUS SOLUTIONS OF GLYCINE AND α-ALANINE; A COMPARISON BETWEEN LITERATURE DATA AND THE DATA OF THIS PAPER

Concn., c., g./100 ml. soln.	Glycine			Alanine	
	1	6	(7.193)		
Molality	0.1344	0.8275	1.0000	1.0000	
Relative viscosity	1°	1.0142 <sup>a</sup>	1.1020 <sup>a</sup>	(1.1271) <sup>a</sup>	
	18°	.....	.....	1.153 <sup>c</sup>	
	25°	{ 1.0193 <sup>d</sup>	{ 1.1265 <sup>d</sup>	{ 1.1549 <sup>d</sup>	1.2874 <sup>d</sup>
	35°	{ 1.0205 <sup>b</sup>	{ 1.1230 <sup>b</sup>	{ 1.1470 <sup>b</sup>	1.2705 <sup>d</sup>

<sup>a</sup> Lyons and Thomas: value in parentheses refers to concentration slightly beyond that for which equation is claimed to be valid. <sup>b</sup> From the interpolation formula of Lyons and Thomas. <sup>c</sup> Hedestrand. <sup>d</sup> This paper.

where  $E^*$  is the activation energy for viscous flow expressed in calories per mole. For a given liquid A, with a high degree of ordering of its molecules

due to van der Waals forces or to specific valency forces such as hydrogen bonding,  $E_A^*$  might be expected to be of greater magnitude than  $E_B^*$  for a liquid B in which a lesser degree of ordering obtains. Since entropy is related to structural order, the differential entropies of dilution ( $\bar{S}_1 - \bar{S}_1^0$ ) may be interpreted as indicating the strengthening or weakening effects of solute amino acids on the quasi-solid structure of water.  $\bar{S}_1 - \bar{S}_1^0$  as a function of molality concentration may be expressed by an equation of the form<sup>13</sup>

$$\bar{S}_1 - \bar{S}_1^0 = km^2$$

Only in the case of glycine does  $k$  in the above expression have a positive value, *i.e.*, glycine weakens the structure of water.

Lyons and Thomas<sup>27</sup> have discussed a number of properties of aqueous solutions of glycine in terms of the structure-weakening effect of glycine on the solvent.

If the assumption is made that the Arrhenius equation is valid over a short temperature range, say 25–35°,  $E_{H_2O}^*$  may be calculated providing that reliable values are known for the viscosities of water at these temperatures. In view of the discussion above

$$\Delta E^* = E_{H_2O}^* - E_{soln}^*$$

should parallel in sign the differential entropies of dilution.

Values for the calculated quantity  $\Delta E^*$ , the differential activation energy for viscous flow, are tabulated in Table V for the concentration range for which the differential entropies of dilution have been computed, and are shown plotted in Fig. 1. Of the five amino acids investigated in this work, only for glycine has  $\Delta E^*$  been found to have a positive value.

The quantity  $\Delta E^*$  is fairly well expressed as a function of concentration by the equation

$$\Delta E^* = Am + Bm^2 + Cm^3 + \dots$$

Values for the constants in the above expression are given in Table VI.

TABLE VI  
CONSTANTS FOR THE EQUATION:  $\Delta E^* = Am + Bm^2 + Cm^3 + \dots$

Amino acid	A	B	C	D
Glycine	47.4	12.92	0.288	0
$\alpha$ -Alanine	-285.6	43.15	0.876	0
$\beta$ -Alanine	-147.8	64.78	-17.05	1.30
$\alpha$ -Amino- <i>i</i> -butyric	-616	137	0	0
$\alpha$ -Amino- <i>n</i> -valeric	-544	-1.62	0	0

In Fig. 1 it will be noted that the relative positions of the curves representing  $\Delta E^*$  correspond to the relative positions of the curves representing  $\bar{S}_1 - \bar{S}_1^0$ ; *e.g.*, at the higher concentrations the curves for  $\beta$ -alanine lie above those for  $\alpha$ -alanine, and both curves for these two acids lie intermediate between the corresponding curves for glycine and the curves for both  $\alpha$ -amino-*i*-butyric acid and  $\alpha$ -amino-*n*-valeric acid. Aside from the agreement in sign, strict parallelism between  $\Delta E^*$  and  $\bar{S}_1 - \bar{S}_1^0$  does not exist for the entire range of concentration considered. It will be noted, for example, that for concentrations up to slightly beyond 0.4 molal,  $\bar{S}_1 - \bar{S}_1^0$  for  $\alpha$ -alanine is greater than for  $\beta$ -alanine whereas the opposite is true for  $\Delta E^*$ . It will also be noted that at all concentrations the spread between  $\Delta E^*$  for  $\alpha$ - and  $\beta$ -alanine is much greater than the spread between  $\Delta E^*$  for  $\alpha$ -amino-*i*-butyric acid and  $\alpha$ -amino-*n*-valeric acid whereas again the opposite is true for  $\bar{S}_1 - \bar{S}_1^0$ . In general, however, Fig. 1 indicates the existence of the correlation suggested.

Correlation of  $\Delta E^*$  with  $\bar{S}_1 - \bar{S}_1^0$  calculated from heats of dilution at 25° might be more demonstrable if viscosity data were available at 20 and 30°, and if, for amino acids as yet uninvestigated, both  $\Delta E^*$  and  $\bar{S}_1 - \bar{S}_1^0$  be found to have positive values.

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## Polarography of Carbonyl Compounds. I. Linear Unsaturated Conjugated Molecules

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Polarographic data for benzaldehyde, acetophenone, crotonaldehyde, acrolein, cinnamaldehyde, benzalacetone and crotylidene acetone in well buffered aqueous and 50% dioxane solution are summarized in this paper.<sup>2</sup> The effects of pH, solvent, liquid junction potentials and ionic strength on the half-wave potentials are discussed. A qualitative statement of the effect of structure in the organic molecule on the half-wave potential is made.

Recently considerable interest has been shown in the relation between the structures and polarographic half-wave potentials of unsaturated aldehydes and ketones. Fields and Blout<sup>3,4</sup> made an

(1) Shell Oil Company, Martinez, California. Most of the data on which this paper is based were taken from a thesis presented by Dale M. Coulson for the degree of Ph.D. at the University of California at Los Angeles, June 1, 1950.

(2) For more complete experimental data order Document 3407 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.20 for photocopies (6 × 8 inches) readable without optical aid.

(3) M. Fields and E. R. Blout, *THIS JOURNAL*, **70**, 930 (1948).

(4) M. Fields and E. R. Blout, private communication.

extensive study of the polyene aldehydes,  $CH_3-(CH=CH)_j-CHO$ , where "j" was 1 through 5. They used 50% dioxane as the solvent and several buffers that give effective buffering in the pH ranges for which each buffer was used. A summary of their data is included in Table I. Pasternak<sup>5</sup> studied a number of aryl- and alkyl-unsaturated aldehydes and ketones using 48% ethanol as the solvent. He also used buffering systems that were effective in their respective pH ranges. Since these two sets of data were for different solvents, in order to correlate these data

(5) R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).