

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY, WORCESTER, MASS.]

The Diffusion Coefficients, Densities, and Viscosities of Solutions of Acetamide in Water¹BY HARRY J. CHRISTOFFERS² AND GERSON KEGELES³

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Diffusion coefficients, refractive index increments, densities, and viscosities of aqueous acetamide solutions were measured at 25° over a concentration range from less than 1% to slightly more than 60%. The viscosities and densities of a few solutions were also measured at 20°. The concentration dependence of these and derived quantities has been expressed in empirical equations. The concentration dependence of the diffusion coefficient of acetamide showed an inflection at higher concentrations. Despite a dipole moment twice that of un-ionized acetic acid, acetamide has larger diffusion coefficients with lesser concentration dependence than those for acetic acid.

Introduction

Longworth⁴ and Gosting and co-workers⁵⁻⁷ have observed a correlation between the polarity of the solute and such physical properties as the magnitude of the diffusion coefficient and its concentration dependence as well as the magnitudes of the specific refractive index increment and the partial specific volume of the solute in aqueous solutions of a number of amino acids and their isomeric hydroxyamides. With the exception of a single experiment upon each of the isomers of alanine,⁴ it was found that the more polar isomers had lower diffusion coefficients and coefficients which were more concentration dependent.

Gutter and Kegeles⁸ and Donoian and Kegeles⁹ made extensive studies of the diffusion in water of α -alanine and β -alanine, respectively. Their studies revealed that in the case of these two isomers, the substance of greater polarity also had the larger diffusion coefficient and the lesser concentration dependence of the coefficient contrary to the correlation of Longworth and of Gosting and co-workers. Particularly interesting is the comparison of β -alanine with its isomer lactamide studied in detail by Wendt and Gosting.⁷ The magnitudes of the diffusion coefficients at very low concentrations as well as the magnitude of the specific refractive index increment and its concentration dependence are in agreement with the correlation of Longworth and of Gosting, *et al.*, with regard to the polarity of the solute molecules. This is not true, however, for the concentration dependence of the diffusion coefficients. Indeed, the concentration dependence of the diffusion coefficient of lactamide is so much greater than that of β -alanine that there is actually a crossing of the curves at 1.65 molar.⁹

Since the diffusion of un-ionized acetic acid in water has recently been investigated by Vitagliano and Lyons¹⁰ and since the dipole moments of acetamide and monomeric un-ionized acetic acid differ by a factor of about two (3.6 and 1.7 D., respectively¹¹), it seemed desirable to investigate the diffusion of acetamide in water along with other properties of various acetamide-water solutions.

Experimental

Reagent grade acetamide (General Chemical Division, Allied Chemical and Dye Corp.) was crystallized once from hot water in the presence of hydrochloric acid-washed activated charcoal. Be-

fore use, the charcoal was washed first with dilute hydrochloric acid and then with water until no test for chloride ion with silver nitrate could be observed. Also more than 100 ml. of the last washings of the charcoal were evaporated to dryness and no residue of any sort could be observed. The acetamide was then crystallized again from hot 50% aqueous ethyl alcohol and finally twice from hot 95% ethyl alcohol and then dried *in vacuo* over magnesium perchlorate. A small portion which was crystallized again from 95% ethyl alcohol and dried as above did not differ in its diffusion coefficient by more than 0.1% when a solution containing 0.5% solute was allowed to diffuse against water. Therefore the material crystallized twice from 95% alcohol was used for all of the measurements. The purity of the acetamide was further attested to by the fact that the values of the relative fringe deviation function (Ω 's)¹²⁻¹⁴ were less than 5×10^{-4} for diffusion experiments at an average concentration of about 0.25% acetamide by weight.

Doubly distilled water saturated with air was employed as the solvent for this system. All solutions were prepared by weight with internally calibrated weights, and the weighings were corrected to conditions *in vacuo*. A density of 1.159 g./ml. was used for the solid acetamide.¹⁵

Measurements of the diffusion coefficients were made by the Gouy interference method¹⁶⁻¹⁹ using apparatus previously described.^{9,20} The difference in concentration of the two solutions between which diffusion took place was usually about 0.5% by weight. This corresponded to about 60 Gouy interference fringes.

The densities of the liquid solutions were determined with a Reischauer pycnometer and calculated according to the directions of Bauer and Lewin.²¹ Values for the density of pure water were obtained from Dorsey.²²

The viscosities were determined with Ostwald-Fenske size 50 viscometers^{23,24} which had flow times for pure water at 25° of over 300 sec. No kinetic energy corrections were made for the various viscosity determinations. The absolute viscosity of pure water at 20.00° was taken to be 10.019 millipoises as given by Swindells, *et al.*,²⁵ while that at 25.00° was calculated from the 20° value and the datum of Coe and Godfrey²⁶ to be 8.902 millipoises.

Treatment of Diffusion Data.—The data from the diffusion experiments were treated in the conventional manner to obtain preliminary values of the diffusion coefficients^{16,17,19,27} and relative fringe deviation functions (Ω 's).¹²⁻¹⁴

Since a number of the diffusion experiments, particularly at the higher concentrations, gave values of the relative fringe deviation function which increased or decreased monotonically over the whole range of experimental values of $f(z_i)$ between 0 and 1 and were usually larger in absolute magnitude on an

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TABLE I
 RESULTS OF GOUY EXPERIMENTS

Av. wt. % acetamide	Average molarity	$D \times 10^7$, cm. ² /sec. at 25.135°	$D \times 10^7$, cm. ² /sec. calcd. for 25.00°	Δt , sec.	Δw	$\frac{\Delta n}{\Delta w}$	$\frac{\Delta n}{\Delta c}$
0.2583	0.04360	124.90 ± 0.02	124.44	68.5	0.5166	0.001132	0.006713
0.2585	.04363	124.94 ± .04	124.48	75.1	.5169	.001131	.006702
2.5664	.4339	120.37 ± .04	119.92	62.3	.4881	.00114	.00677
5.1060	.8646	116.00 ± .14	115.56	47.5	.5573	.00115	.00679
10.3532	1.7593	106.92 ± .08	106.51	68.5	.5301	.00117	.00689
14.7712	2.5177	101.89 ± .10	101.49	67.6	.5719	.00114	.00669
20.4347	3.497	95.73 ± .03	95.35	-97.9	.5207	.00117	.00681
30.0658	5.179	86.79 ± .14	86.43	28.9	.4229	.00117	.00677
40.0774	6.948	78.00 ± .05	77.66	29.7	.5630	.00120	.00689
48.4	8.44	70.83 ± .13	70.50	74.0
58.9411	10.322	59.68 ± .06	59.38	116.7	0.3634	0.00116	0.00660
63.8273	11.185	56.58 ± .09	56.29	124.1	0.1822	0.00115	0.00658

average for pictures taken during the latter part of an experiment, it was suspected that the value of the δ -correction for the location of the undeviated slit image position may have been in error.

An empirical procedure was thus adopted to make small adjustments in the experimental δ -correction and j_m values to minimize the relative fringe deviation functions near the end points ($f(z_i) = 0$ or $f(z_j) = 1$). This was done by choosing values of the δ -correction slightly different from the experimental values and calculating the relative fringe deviation functions for the last pictures until a best value was found. Then, slight variations in j_m were used to calculate the relative fringe deviation functions for the early pictures using the best value of the δ -correction found for the last pictures. The process was iterated until no improvement was apparent. Very often the fractional portion of the j_m value so determined agreed more closely with that calculated from the Rayleigh interference pattern taken using the whole diffusion channel and the reference channel at the end of the experiment than with the fractional fringe taken using the double slit Rayleigh pattern at the beginning of the experiment between the two solutions in the diffusion channel.

The diffusion coefficients were all determined at 25.135°. The values were corrected to 25.00° by use of the equation $D\eta/T = \text{const.}$ The viscosities of the solutions at the two temperatures were calculated by use of the equation $\eta = Ae^{B/T}$. The value of B was obtained from an empirically determined equation relating B to the mole fraction of acetamide in the solution.

Results

The results obtained from the diffusion experiments are presented in Table I. In the first column are presented the average weight per cent values of acetamide of the upper and lower solutions. The average concentrations in moles per liter calculated from weight per cent data, density data, and a value for the molecular weight of acetamide of 59.07 are given in column 2. In column 3 the diffusion coefficients along with the average deviation from the mean of the results calculated from each Gouy picture are given for the experimental temperature of 25.135°. Usually each experiment was based upon six to nine pictures; the experiment for 58.94 weight % was, however, based only upon three pictures due to failure of the thermostat to function properly after the third picture. The diffusion coefficients corrected to 25.00° are given in column 4. In column 5 are given the zero time corrections. The negative value for Δt for the 20.43 weight % experiment was probably due to a small amount of leakage through the stopcock used on the boundary-sharpening siphon before it was checked at the time of removal of the siphon. Column 6 gives the difference in concentration between the upper and lower solutions in terms of weight per cent. Values of the specific refractive index increment, $\Delta n/\Delta w$, are listed in column 7 while column 8 lists values of the molar refractive index increment, $\Delta n/\Delta c$, where c refers to the concentration in moles per liter of acetamide.

Empirical equations²⁸ relating the diffusion coefficients to the molar concentration of acetamide were

determined with the aid of an I.B.M. Model 650 digital computer using a program entitled, "Weighted Least-square Polynomial Approximation, I.B.M. File Number 6.0.009." While too much significance should not be attached to the equations except as a means for interpolation between experimental points and extrapolation to zero concentration, the equations of lowest degree which reproduced the data within 0.2% were

$$10^7 D_{25.135} = 125.39 - 10.958c - 1.2742c^2 + 1.5729c^3 - 0.4669c^4 + 0.06563c^5 - 0.004499c^6 + 0.0001206c^7$$

$$10^7 D_{25.00} = 124.93 - 10.938c - 1.2661c^2 + 1.5684c^3 - 0.4659c^4 + 0.06551c^5 - 0.004492c^6 + 0.0001204c^7$$

An empirical equation which relates $\Delta n/\Delta w$ to the molarity within 2% of the experimental values is given by

$$\Delta n/\Delta w = 1.134 \times 10^{-2} + 1.350 \times 10^{-5}c - 1.057 \times 10^{-6}c^2$$

In Table II are presented the results of the experimentally determined densities and viscosities as a function of the concentration of acetamide in the various solutions along with the apparent molar volume of the acetamide in the solution. In those cases for which measurements upon the same solutions were made at both 20 and 25°, there are listed average increments for the change in density per degree over the five degree interval and also the value of the quantity B calculated for the five degree interval from the equation

$$B = \frac{(293.16)(298.16)}{5} \ln \frac{\eta_{20}}{\eta_{25}}$$

Empirical equations were obtained by the least-squares computer program mentioned earlier for the relationships between these quantities and various functions of the concentration. The following equation reproduces the density values as a function of molality at 25.00° within 0.05%, except for the density of the 8.422% solution which is reproduced within 0.1%

$$\rho_{25.00} = 0.99704 + 3.6119 \times 10^{-3}m - 7.4639 \times 10^{-5}m^2 - 9.6152 \times 10^{-6}m^3 + 8.4758 \times 10^{-7}m^4 - 2.6046 \times 10^{-8}m^5 + 2.7707 \times 10^{-10}m^6$$

An equation in terms of the molality which reproduces the values of the apparent molar volume in ml. at 25° to within 0.3% for all but the lowest two concentrations (2% for the lowest and 1% for the next to the lowest) is given by

$$\phi V_{25} = 56.505 - 0.7341m + 0.1329m^2 - 9.72 \times 10^{-3}m^3 + 3.040 \times 10^{-4}m^4 - 3.343 \times 10^{-6}m^5$$

The equation of lowest degree in the molarity for the viscosity in millipoises which represents the results for

(28) Acknowledgment is gratefully made to Dr. Charles N. Caughlan of Montana State College for his generosity in furnishing the program and computer time for the derivation of all empirical equations.

TABLE II
 RESULTS OF DENSITY AND VISCOSITY EXPERIMENTS

Wt. % acetamide	Data for solutions at 25.00°			Data for solutions at 20.00°			Data for temp. effect over interval 20 to 25°	
	Density, g./ml.	Appar. molar vol. of acetamide, ml.	Viscosity, millipoises	Density, g./ml.	Appar. molar vol. of acetamide, ml.	Viscosity, millipoises	$-(\Delta\rho/\Delta t) \times 10^4$, g./ml./deg.	B defined by $\eta = Ae^{B/T}$
0.5862	0.99723	58	8.986	0.99859	56	10.119	2.72	2076
1.4179	0.99790	56	9.130	0.99914	55	10.284	2.48	2081
8.422	1.00230	55.6	10.456	1.00386	55.2	11.828	3.12	2155
9.835	1.00345	55.4	10.775					
18.903	1.00972	55.32	12.907	1.01170	55.01	14.686	3.96	2257
20.108	1.01063	55.29	13.244					
30.474	1.01779	55.29	16.535					
39.557	1.02378	55.34	20.370					
49.074	1.02951	55.44	25.707					
60.230	1.03492	55.65	34.57					
60.829	1.03496	55.68	35.14	1.03843	55.41	41.744	6.94	3010

25.00° with a precision of 0.3% is given by

$$\eta_{25} = 8.918 + 1.0008c + 4.913 \times 10^{-2}c^2 + 8.618 \times 10^{-3}c^3 - 5.708 \times 10^{-4}c^4 + 5.025 \times 10^{-5}c^5$$

Since only five different solutions were investigated at 20.00° as well as at 25°, the following equations should be considered of quite limited validity. They are: for the density in terms of the molality

$$\rho_{20} = 0.99823 + 3.745 \times 10^{-3}m - 7.976 \times 10^{-6}m^2 - 1.1612 \times 10^{-6}m^3 + 3.765 \times 10^{-8}m^4$$

for the apparent molar volume in terms of the molality

$$\phi V_{20} = 55.52 - 0.1590m + 0.00589m^2$$

for the viscosity in terms of the molality

$$\eta_{20} = 10.00 + 1.162m + 7.06 \times 10^{-3}m^2 - 2.036 \times 10^{-4}m^3$$

for the density increment per degree in terms of molality

$$-(\Delta\rho/\Delta t)10^4 = 2.39 + 0.447m - 0.0104m^2$$

and for the viscosity B value in terms of mole fraction

$$B = 2072 + 2815N + 319.0N^2$$

Discussion

It is of interest to observe that the apparent molar volume goes through a minimum at a solute concentration of about five molar as does that of dimethylacetamide.²⁹ The decrease in the apparent molar volume

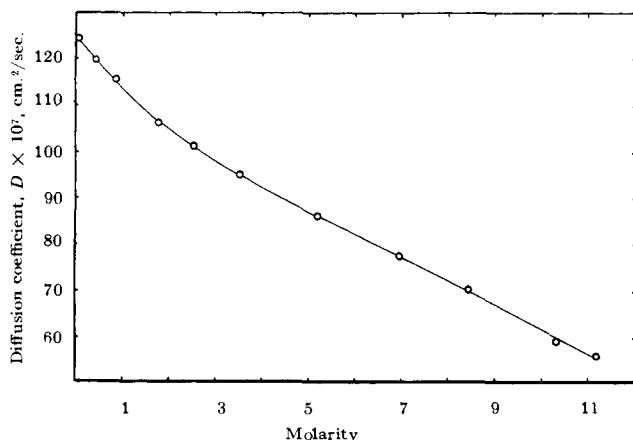


Fig. 1.—The concentration dependence of the diffusion coefficient of acetamide in water at 25.00°.

with increasing concentration might possibly be interpreted as being due to a "loosening" of the hydrogen bonded structure of water in very dilute solutions followed by a filling up of the holes in the liquid as the concentration is increased. Finally, a further breakdown of the quasi-crystalline structure of water might occur at relatively high concentrations of acetamide.

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Assuming this interpretation, one might speculate one step further by saying that this behavior of the apparent molar volume for the acetamide and dimethylacetamide in water, in contrast to the linear dependence of the apparent molar volumes of some amino acids and their isomeric hydroxyamides,³⁰⁻³² is due to the lesser tendency of acetamide and dimethylacetamide to form more than one hydrogen bond per molecule. Thus, an acetamide molecule provides a chain-ending unit for a group of water molecules while an amino acid or hydroxyamide molecule may act as a chain-continuing unit in dilute solutions.

Wendt and Gosting⁷ have observed a correlation between the concentration dependence of the apparent molar volume and the specific refractive increment in the comparison of lactamide with α -alanine. Such an observation seems to be valid for the acetamide-water system also insofar as there is a minimum in the apparent molar volume at a concentration of about five molar and a maximum in the specific refractive increment at a concentration of about six molar.

Donoian and Kegeles⁹ observed a definite inflection in the curve describing the concentration dependence of the diffusion coefficient of β -alanine. An inflection is also definitely present in the curve describing the concentration dependence of the diffusion coefficient of acetamide (Fig. 1). It seems reasonable that such an inflection in the diffusion coefficient curve might be the result of the difference between several competing processes of roughly equal magnitude so that any interpretation of this inflection would require a more detailed knowledge of the system than is presently available. Thus, if information concerning the activity coefficients and the self-diffusion coefficients of the two components were available, one might attempt an interpretation similar to that made by Irani and Adamson³³ for the sucrose-water system.

In comparing the diffusion coefficients of acetic acid and acetamide, the following observations might be made. The absolute magnitude of the diffusion coefficient of acetamide at infinite dilution (124.93) is 4% larger than that of acetic acid (120.1) at 25°. The ratio of the diffusion coefficient at a concentration of 9.75 moles of solute per liter of solution to the value at infinite dilution for acetamide is 62.71/124.93 or 0.502 while that for acetic acid¹⁰ is 57.85/120.1 or 0.482, or a difference of about 4% less change for acetamide than for acetic acid. Both of these effects are in the opposite direction to those observed by Longworth⁴ and Gosting and co-workers⁵⁻⁷ with respect to their correlation of

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these properties with the relatively large dipole moment differences between amino acids and their isomers. One would expect the oxygen of the -OH group in the acetic acid molecule to undergo hydrogen bonding more

readily than the nitrogen of the -NH₂ group in the acetamide molecule. This may possibly be an explanation of the differences in the behavior of aqueous solutions of these two molecules.

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On the Standard Potential of the Titanium(III)-Titanium(II) Couple

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Data on the potential of the Ti(III)-Ti(II) couple are given and evaluated. These data support the theoretical value of approximately -2 v. *vs.* the n.h.e. as the reduction potential of the couple in aqueous solution.

The standard potential of the Ti(III)-Ti(II) couple is given by Latimer¹ as -0.37 v. based upon measurements reported by Forbes and Hall² using a mercury pool cathode on solutions thought to contain Ti(II) in 0.1 M HCl. Other authors^{3,4} have been completely unable to prepare stable solutions of Ti(II) not only in aqueous solutions but in low-acidity solvents including acetonitrile and dimethylformamide and have concluded that Ti(II) quickly disproportionates to Ti(III) and Ti(0). We have attempted to clarify this question by polarographic measurements in aqueous and nonaqueous media.

Experimental

Mixed titanium(II) and titanium(III) halides were prepared according to the procedure described by Forbes and Hall.² Aqueous or acetonitrile solutions to be polarographed were prepared by suspending the mixed halides in cold, deaerated solvent and (in a closed nitrogen flushed system) filtering directly into an ice-cold deaerated polarographic cell.

Hexaaquatitanium(III) chloride was prepared by dissolving C.P. titanium in concentrated hydrochloric acid in a hydrogen atmosphere. The crystals were collected and dried in a nitrogen stream and stored in a vacuum desiccator.

Titanium hydride, Grade E, was obtained from Metal Hydrides, Inc. Titanium monoxide, brass-colored, was prepared by the method of Dawihl and Schroter.⁵

Acetonitrile was dried and purified by distillation from P₂O₅ until a residual current wholly attributable to capacitive charging current was obtained. Polarographic grade tetraethylammonium bromide (Southwestern Analytical Chemicals) was used in acetonitrile when a supporting electrolyte was desired. All reagents used as dissolution agents, complexing agents, or supporting electrolytes in aqueous solution were analytical grade.

Polarograms were obtained using a Sargent Model XXI polarograph without damping. The saturated calomel electrode was used as reference. The reference was connected to the polarographic cell *via* a 1 M KCl salt bridge through a 6-mm. length of porous 6-mm. diameter Vycor rod. Water diffusion into a polarographic cell containing acetonitrile as solvent was felt to be neglectable during the course of a single polarogram. All solutions were deaerated with prepurified tank nitrogen.

Results and Discussion

Polarograms of solutions prepared by the procedure of Forbes and Hall² are shown in Fig. 1. The wave at -0.2 v. is for the oxidation Ti(III) → Ti(IV) + e⁻, while the wave at -0.7 v. is for the irreversible reduction Ti(IV) + e⁻ → Ti(III). Curve II is exactly the polarogram obtained when hexaaquatitanium(III), a labile complex, is polarographed, showing conclusively

that Ti(III) does not reduce in this medium at a potential more positive than that at which H⁺ is reduced. If Ti(II) existed in such solutions, absence of an anodic wave for the oxidation of that Ti(II) requires that Ti(II) be oxidized irreversibly by at least 0.8 v. If the potential -0.37 v. for the couple were valid the couple would be highly irreversible and not obey the Nernst equation as previously reported.² The potential measured at zero current by Forbes and Hall was limited on the negative side by reduction of H⁺ rather than reduction of Ti(III) and on the positive side by oxidation of Ti(III) rather than oxidation of Ti(II) and actually represented a mixed potential between those limiting processes. The potential of a mercury cathode in contact with this solution in a potentiometric determination where no current is drawn would depend upon the rates of electrochemical reduction of hydrogen ion and oxidation of titanium(III). That potential would approximate the polarographic zero current in curve II.

Of sixteen trials by Forbes and Hall, ten were discarded because of rapidly falling potentials and reducing capacity less than for Ti(III) alone. The relationship between falling potential and low reducing capacity can be seen from curve III of Fig. 1 since as Ti(IV) is formed the potential of the Hg cathode at zero current falls into the potential range in curve III giving only residual current, a potential more positive than in curve II. Reducing capacity greater than for Ti(III) alone on the remaining six trials suggests the presence of colloidal Ti(0) from disproportionation of Ti(II). Groves and Russell⁶ have deposited finely divided titanium on Hg cathodes at high current densities and found such titanium reacts quickly and quantitatively with dichromate (the test used by Forbes and Hall for reducing capacity).

Polarograms of solutions prepared by dissolving titanium metal, TiH₂, or TiO in mineral acids directly in deaerated polarographic cells showed waves only for Ti(III). Polarograms of Ti(III) in complexing media such as 1 M oxalate, citrate, and thiocyanate at elevated pH where H⁺ reduction would not interfere showed no reduction of Ti(III). For example, in 1 M citrate ion at pH 7, Ti(III) could be investigated to -1.8 v. *vs.* s.c.e. without evidence of reduction, at which point electrolyte reduction occurs in the absence of titanium(III). The magnitude of the shift in half-wave potential for Ti(III) as the citrate complex, though indeterminate, is probably several tenths of a volt.

In dry acetonitrile, both hexaaquatitanium(III) chloride and dry mixed titanium halides prepared by the method of Forbes and Hall give similar two-step polarograms with an initial reduction wave at -1.3 v. *vs.* s.c.e. The second step is at a more negative poten-

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