

DETERMINATION OF ACTIVITY COEFFICIENTS OF
AMMONIUM FORMATE IN AQUEOUS SOLUTION
FROM FREEZING POINT LOWERINGS

by

MERLE RAYMOND HUBBARD

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INTRODUCTION

In recent years Dr. H. H. King and Dr. J. Lowe Hall of Kansas State College have been studying the application of Gibbs' adsorption equation to solutions of ammonia derivatives of salts of fatty acids in the solvent, liquid ammonia. In the Gibbs adsorption equation, activities of these salts should be used in place of concentration. The observation that liquid ammonia, used as a solvent, exhibits many properties similar to water has led to the desire to know how salts of the fatty acids will act in a water solution. Ammonium formate was chosen as an example of fatty acid salts for this investigation. The freezing point lowering method for determining the activity coefficient was chosen because of its accuracy and comparative simplicity of procedure.

DESCRIPTION OF APPARATUS

The freezing point apparatus (Fig.1) was similar to that used by Adams (1). It consisted of a large galvanized iron container well insulated from radiation and adsorption of heat by a one and one-half inch layer of wool felt. Two metal cylinders, each holding a one-liter unsilvered pyrex Dewar flask, were placed in the large container.

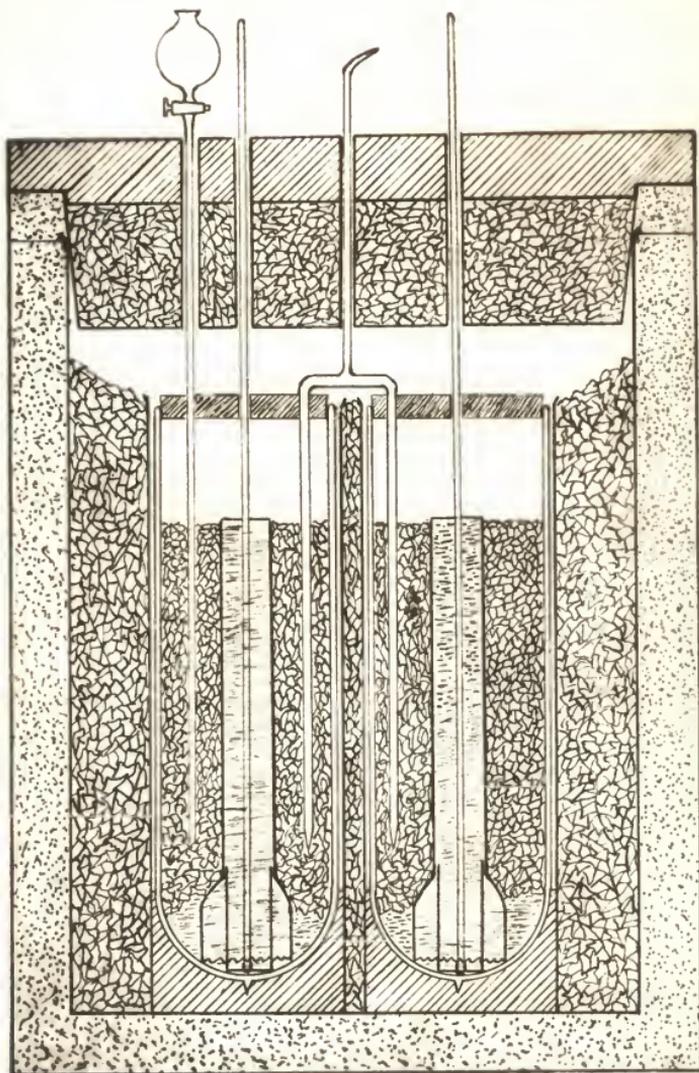


Fig. 1.

Two pumps were used for stirring the solution in the flasks. The solutions were circulated from the bottom of the flasks to the surface of the liquids. Stirrer barrels were made of one-half inch pyrex tubing. The length of the stirrer barrels was approximately eight inches, and the three inches at the bottom were flared. The stirrer pistons were cylinders of gold-plated brass, closed at the lower end, and fastened to long 3 mm. glass rods. This stirring method completely mixed the solutions about three times per minute. The stirrers were operated by a motor.

The cover for the apparatus was a pan covered with a one and one-half inch wooden top. Metal tubes were placed in this cover at proper positions for supporting the stirrers, thermo-element leads, and a pipette used to remove samples from the ice-solution flask.

A 24-junction copper-constantan thermo-element (2), made in halves of twelve junctions each, was used for determining temperature differences between the ice-water in one Dewar and ice-solution in the other. Five No. 30 double silk-covered constantan wires in parallel were soldered to one No. 36 enameled copper wire. Each junction was insulated with bakelite varnish. The whole bundle was bound together, shellacked, and dried in an oven. Each of the two arms was inserted into a glass tube sealed at

one end, and the tubes then were filled with molten naphthalene. The part not encased in naphthalene, from which leads were taken, was insulated with paraffin, bound with silk tape, and shellacked to make it water-proof.

The thermal was calibrated by determining the freezing point lowerings produced by small concentrations of mannite in water, as described by Hall and Harkins (3). The equation which represents the performance of the element is

$$E = 913.04t + 11.6486t^2 + 1.1075t^3.$$

A Zeiss laboratory type interferometer (4) was used to determine the concentration of the solutions. When the 2 cm. cell was used, one interferometer scale division was equivalent to 0.000139 molal ammonium formate.

The temperature differences between the ends of the thermo-element were determined by measuring the electromotive force with a Leeds and Northrup potentiometer and galvanometer. This apparatus is accurate to 0.0001° C.

PREPARATION OF MATERIALS

The ammonium formate was obtained from the Eastman Company. Its extreme hygroscopic nature necessitated thorough drying. This was done in a vacuum desiccator, over sulphuric acid.

Solutions used in calibrating the interferometer were made by placing the approximate amount of formate in

previously dried and weighed weighing bottles, weighing the same, and adding the necessary weight of water to make the solution of desired concentration. This procedure gave little chance for the formate to absorb moisture.

The ice used in the ice-water and in the ice-solution flasks was made from distilled water frozen in aluminum trays in an electric refrigerator. The ice was prepared for the flasks by crushing it in clean cotton cloths to a size of about 10 mm. and washing it with previously cooled distilled water.

EXPERIMENTAL PROCEDURE

Ordinary crushed ice was placed around the two cans in which the Dewar flasks were to be placed. The stirring pumps were placed in the Dewars and 600 grams of finely crushed ice, prepared as previously described, were added to each Dewar, care being taken that no ice got into the stirring tubes. Distilled water was added to each Dewar until the level of the solution was about one-eighth inch below the top of the stirrer tubes. As the solute is not volatile, no precaution was taken to remove air from the water.

The Dewars were then placed in the apparatus, the cork stoppers for each were adjusted, and the thermo-element

was inserted. The top was lowered over the stirring rods and thermo-element leads. The sampling pipette was lowered into the flask which was later to contain the ice-solution. The top was filled with ice, and the stirrers set in motion. The thermo-element leads were connected to the potentiometer and the whole apparatus allowed to stand for two or three hours. At the end of that time the potentiometer was balanced and a reading taken to determine whether the ice-water solution in each Dewar was at constant temperature and if the temperatures were equal. This temperature was taken to be 0° C. No difficulty was encountered in obtaining this state of equilibrium. When it was reached the potential from the thermo-element was zero.

At this point of the procedure the water was removed from one Dewar with the sampling pipette. The stirrers were kept in operation. The water withdrawn from the one flask was replaced with an equal volume of a solution of ammonium formate, made to a concentration approximately equal to that of the highest concentration desired for a series of points. This solution was previously cooled in an ice-salt bath until ice began to form.

Stirring was continued for thirty minutes. Then the electro-motive force readings were taken with the poten-

tiometer, and were repeated until they became constant. A constant electro-motive force indicated a state of equilibrium in the ice-formate solution.

Fifty cc. or more of the solution was withdrawn from the solution flask into the stationary pipette and removed from it by means of a dry pipette to a 125cc. Erlenmeyer flask and the flask immediately stoppered. The quantity of solution withdrawn depended on the concentration interval desired. The volume of solution removed was replaced with an equal volume of distilled water, cooled to the freezing point. The water added diluted the solution in the flask to give a second experimental point, and also rinsed the sampling pipette. The solution was drawn up into the pipette and allowed to return to the flask several times during each stirring period in order to eliminate the error which might come from any water or more concentrated solution remaining in the sampling pipette. This procedure for obtaining experimental points was repeated four to eight times, depending upon the concentrations being used in each run. It was impractical to obtain a larger number of points, due to an unstable equilibrium caused by the reduced quantity of ice.

The solutions were allowed to come to room temperature and their concentrations determined by means of the inter-

ferometer. Two or three cc. of each solution were placed in a small weighed Erlenmeyer flask and accurately weighed. Distilled water was immediately added and the flask was reweighed. The unknown solutions were thus diluted by weight to concentrations ranging between 0.001 M and 0.01 M. At these concentrations they could be compared directly with water in the interferometer and the exact concentrations determined. The concentration of the original solution was calculated from the concentration of the diluted solutions and the amount of water added. This method eliminated the difficult task of making a standard solution to within 0.01 M. of each unknown solution.

CALCULATION OF ACTIVITY COEFFICIENTS

A method for calculating the activity coefficients of electrolytes, based upon the freezing point depression, partial molal heat contents, and heat capacities of their solutions, has been developed by Lewis and Randall (5). As thermal data is not available for ammonium formate, only tentative activity coefficients, γ' , can be calculated at present. Lewis and Randall have shown (5) that thermal effect corrections do not change the values of γ' of sodium chloride appreciably in dilute solutions and not more than 3% in 1.00 M solutions.

We do not believe the values of the activity coefficients of ammonium formate are appreciably affected by disregarding thermal data in the Lewis and Randall equation.

Lewis and Randall (5) give the equation

$$\log \gamma' = \int_0^m -j d \log m - \frac{j}{2.303} + \frac{0.00025}{\nu} \int_0^m \frac{t}{m} dt$$

in which t is the depression of the freezing point, m is the concentration in grams of solute per thousand grams of water, ν the number of ions in which an electrolyte dissociates (in this case, two) and $j = 1 - t/1.858\nu m$. This formula applies to all solutions above 0.01 M.

Log m was plotted against j and the area under this curve was measured with a planimeter. These areas between experimental points give the values of the first integral, $\int_0^m -j d \log m$, between the concentration limits of 0.01 M and 1.00 M. The value for this integral will be called A .

The value for A from infinite dilution up to 0.01 M was obtained by the formula

$$\int_0^m -j d \log m = - \frac{B}{2.303\alpha} (.01)^\alpha$$

where α and B are constants obtained by the formula

$j = \beta m^\alpha$, or $\log j = \log \beta + \alpha \log m$. If $\log j$ is plotted against $\log m$, α is the slope of the line and β is the intercept on the axis of $\log j$. We obtain the final values

of the integral by adding the value for A up to 0.01 M, to the values already determined for A up to 1.00 M.

Values for the second definite integral, $\frac{0.00025}{\nu} \int_0^m \frac{t}{m} dt$, were obtained by plotting t/m against t , and measuring the areas under the curve between each of the experimental points. The values of this integral (B) are so small until a molality of 0.50 M is reached, that they may be disregarded in the final calculation. Values for A and B are given in Table II.

Values of the activity coefficients up to 0.01 M were calculated by the formula

$$\log \gamma' = - \frac{\beta(\alpha+1)m^\alpha}{2.303\alpha}$$

where α and β are defined the same as before. For ammonium formate α had the value of 0.5333, and β the value of 0.6998.

DISCUSSION OF RESULTS

Figure 2 is a plot of the freezing point lowering, Δt , against the molality. The experimental points all fall very near to this curve. Any small variation from this curve, if only 0.002 of one degree will cause a large error in the t/m term. A comparison of columns one and three

of Table I shows this error. A large graph of this curve was made and each point which was not on the curve was corrected as to temperature. Results of this correction are given in the sixth column of Table I. The temperature determinations involved more factors which might cause error than did the concentration determinations. The concentrations were therefore considered correct.

Figure 2 is a plot of the molal lowering, t/m , against m . Table II gives the values of the parts of the equations used in calculating γ' . Table III gives the values of $-\log \gamma'$, and final values of γ' , for each experimental concentration.

Jones and his co-workers (6), and Gitman (7) show that the molal depression of the freezing point of a wide variety of solutes passes through a minimum value as the concentrations of their solutions are increased. The concentration at which this usually occurs is in the neighborhood of 0.20 M. They suggested that the dissolved substance probably undergoes hydration in solution. Thus, as the concentration of the solution increased, less and less water remained available to function as solvent. A progressive rise in the freezing point depression would be the result.

In the case of ammonium formate, Figure 2 shows that the molal depression change is very rapid until a concentra-

Table I

Experimental Data			Corrected Data		
m	t	t/m	m	t	t/m
1.00000*	3.13875	3.1387	1.00000*	3.13875	3.1387
0.90000*	2.83500	3.1500	0.90000*	2.83500	3.1500
0.79945	2.53225	3.1674	0.79945	2.53090	3.1657
0.69526	2.20328	3.1690	0.69526	2.20648	3.1736
0.62084	1.99069	3.2067	0.62084	1.98124	3.1912
0.56154	1.79281	3.1926	0.56154	1.79686	3.1998
0.52875	1.69081	3.1977	0.52875	1.69216	3.2003
0.49907	1.60108	3.2081	0.49907	1.60108	3.2081
0.45876	1.45755	3.1771	0.45876	1.47285	3.2105
0.39628	1.28518	3.2431	0.39628	1.27980	3.2295
0.36281	1.18226	3.2586	0.36281	1.17315	3.2334
0.32166	1.04719	3.2556	0.32166	1.04355	3.2442
0.26954	0.86389	3.2051	0.26954	0.87750	3.2555
0.19479	0.62476	3.2074	0.19479	0.63727	3.2727
0.13943	0.45435	3.2587	0.13943	0.45900	3.2927
0.05479	0.18734	3.4193	0.05479	0.18225	3.3263
0.04075	0.13332	3.2716	0.04075	0.13616	3.3415
0.03000*	0.10092	3.3640	0.03000*	0.10092	3.3640
0.01500*	0.05265	3.5100	0.01500*	0.05265	3.5100
0.01000*	0.03556	3.5563	0.01000*	0.03556	3.5563
0.00600*	0.02160	3.6000	0.00600*	0.02160	3.6000

*Interpolated values.

Table II

m	t/m	j	log m
1.00000	3.1387	0.15537	0.000000
0.90000	3.1500	0.15237	-1.954240
0.79945	3.1657	0.14811	-1.902790
0.69526	3.1736	0.14599	-1.842150
0.62084	3.1912	0.14125	-1.792980
0.56154	3.1998	0.13896	-1.749380
0.52875	3.2003	0.13881	-1.723250
0.49907	3.2081	0.13670	-1.698160
0.45876	3.2105	0.13606	-1.661580
0.39628	3.2295	0.13095	-1.598030
0.36281	3.2334	0.12990	-1.559680
0.32166	3.2442	0.12699	-1.507390
0.26954	3.2555	0.12395	-1.430620
0.19479	3.2727	0.11932	-1.289570
0.13943	3.2927	0.11394	-1.144350
0.05479	3.3263	0.10489	-2.738700
0.04075	3.3415	0.10079	-2.610130
0.03000	3.3640	0.09475	-2.477120
0.01500	3.5100	0.05546	-2.176090
0.01000	3.5563	0.04300	-2.000000
0.00600	3.6000	0.03124	-3.798150

Table III

m	$-\frac{j}{2.303}$	A	B
1.00000	0.06746	0.2446	0.0001900
0.90000	0.06616	0.2375	0.0001600
0.79945	0.06431	0.2300	0.0001400
0.69526	0.06339	0.2211	0.0001200
0.62084	0.06133	0.2141	0.0001100
0.56154	0.06033	0.2081	0.0000980
0.52875	0.06027	0.2039	0.0000920
0.49907	0.05935	0.2005	0.0000860
0.45876	0.05907	0.1962	0.0000780
0.39628	0.05686	0.1873	0.0000660
0.36281	0.05640	0.1819	0.0000590
0.32166	0.05514	0.1758	0.0000520
0.26954	0.05382	0.1666	0.0000420
0.19479	0.05181	0.1496	0.0000290
0.13943	0.04947	0.1278	0.0000220
0.05479	0.04554	0.0842	0.0000062
0.04075	0.04376	0.0714	0.0000043
0.03000	0.04114	0.0530	0.0000027
0.01500	0.02408	0.0305	0.0000007
0.01000	0.01867	0.0223	0.0000003
0.00600	0.01356	-----	-----

Table IV

m	$-\log \gamma'$	γ'
1.00000	0.31187	0.4884
0.90000	0.30350	0.4971
0.79945	0.29417	0.5080
0.69526	0.28437	0.5196
0.62084	0.27532	0.5305
0.56154	0.26833	0.5391
0.52875	0.26407	0.5444
0.49907	0.25976	0.5499
0.45876	0.25519	0.5557
0.39628	0.24419	0.5699
0.36281	0.23824	0.5778
0.32166	0.23088	0.5877
0.26954	0.22037	0.6021
0.19479	0.20138	0.6290
0.13943	0.17724	0.6649
0.05479	0.12974	0.7418
0.04075	0.11516	0.7671
0.03000	0.09414	0.8051
0.01500	0.05458	0.8820
0.01000	0.04097	0.9101
0.00600	0.00573	0.9868

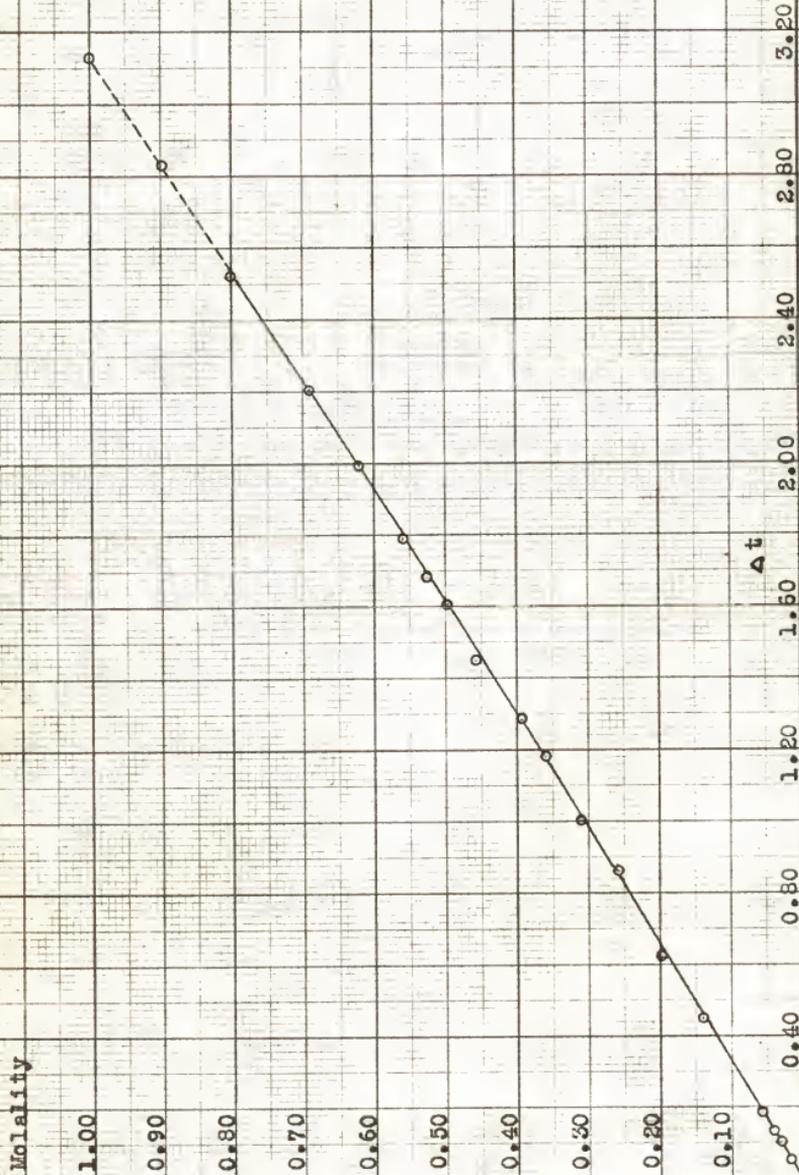


Fig. 2. Molality- Δt depression curve for ammonium formate-water solutions.

2.70

2.60

2.50

 t/m

2.40

2.30

2.20

Molality

0.10

0.20

0.30

0.40

0.50

0.50

0.70

0.80

0.90

FIG. 3. t/m -molality curve for ammonium formate-water solutions.

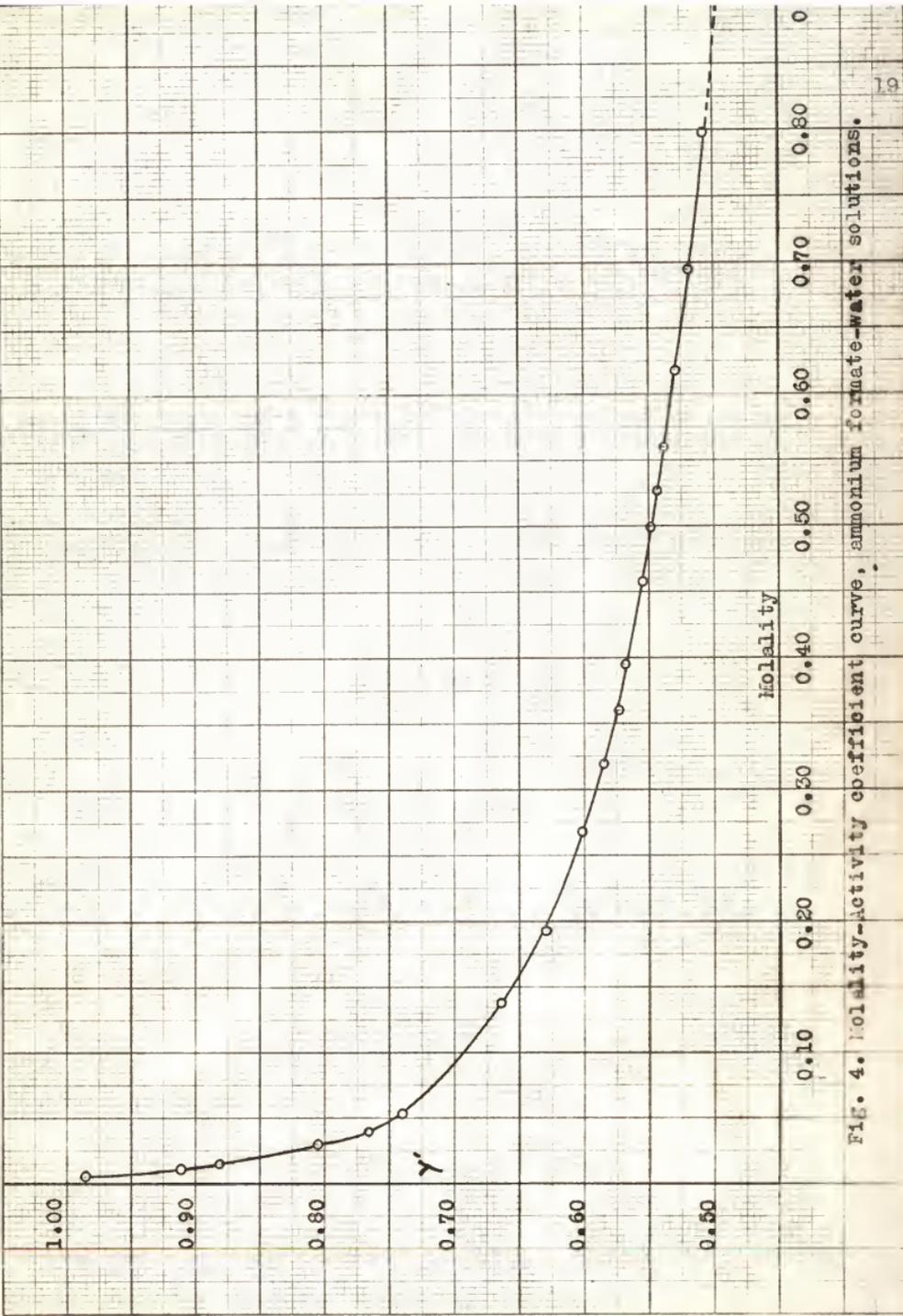


FIG. 4. Molality-activity coefficient curve, ammonium formate-water solutions.

tion of 0.15 M is reached, after which the change is very gradual, approaching a straight horizontal line, and indicating that a minimum value is being reached. We may therefore suppose that ammonium formate undergoes hydration in aqueous solution.

Figure 5 is a plot of activity coefficients γ' , against the molalities of ammonium formate.

SUMMARY

1. Apparatus for determining the freezing point lowering of ammonium formate in aqueous solutions was constructed.
2. A thermo-element was made, and calibrated to an accuracy of 0.0001° , to determine the freezing point depressions.
3. Using the Lewis and Randall equation for utilizing the freezing point lowerings produced by an ionizing solute in water, activity coefficients of ammonium formate in aqueous solutions, between infinite dilution and 1.00 M, were calculated.
4. It is probable that ammonium formate undergoes hydration in aqueous solutions.

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