the theoretical prediction that square root term will be absent for nonelectrolytes.

It is planned to continue the work in this Laboratory by measurements on other salts, at other temperatures, and in other solvents.

Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for the expenses of this investigation.

Summary

1. A new method for the automatic measurement of the time of flow of the liquid in a viscometer of the Ostwald type by means of a photoelectric cell is described. The elimination of the psychological errors inherent in the older technique permits greater precision.

2. The viscosities of dilute aqueous solutions of six salts and two nonelectrolytes have been measured at 25°.

3. The results confirm the prediction made by Jones and Dole based on the Debye theory of interionic attraction that all salts will increase the viscosity of water if measured at sufficiently low concentration, including those salts which give a diminished viscosity at moderate concentrations.

4. The results confirm the Jones and Dole equation for the viscosity of solutions of electrolytes.

5. The results also confirm the Falkenhagen and Vernon equation for the computation of the influence of interionic attraction on the viscosity.

CAMBRIDGE, MASSACHUSETTS

RECEIVED AUGUST 19, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Solubility of Nitrates in Anhydrous Acetic Acid

BY ARTHUR W. DAVIDSON AND HARRIET A. GEER

Introduction

Although several investigations have recently been carried out upon various properties of solutions of salts in anhydrous acetic acid, quantitative solubility data for such solutions are still very meager. Aside from some early work on halides of mercury,[1] calcium and magnesium,[2] and antimony,[3] and the studies of acetates (bases in this solvent) reported from this Laboratory,[4] the only accurate solubility measurements have been those of Seward and Hamblet[5] on potassium perchlorate and potassium nitrate, at a single temperature, in the presence of varying amounts of added salts.

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[1] Étard, *Ann. chim. phys.*, [7] **2**, 555 (1894).

[2] Menschutkin, *Z. anorg. Chem.*, **54**, 89 (1907).

[3] Menschutkin, *J. Russ. Phys.-Chem. Soc.*, **43**, 1785 (1911); *Chem. Abstracts*, **6**, 1280 (1912).

[4] (a) Davidson and McAllister, THIS JOURNAL, **52**, 507, 519 (1930); (b) Davidson and Griswold, *ibid.*, **53**, 1341 (1931).

[5] Seward and Hamblet, *ibid.*, **54**, 554 (1932).

It was mentioned in a previous paper[6] that a large number of nitrates are appreciably soluble in acetic acid. In the present investigation, solubility data were determined over a wide range of temperature for the nitrates of silver, sodium and ammonium, and for barium nitrate at a single temperature. In the case of ammonium nitrate the determinations were continued to the melting point of the pure salt, so as to cover the entire range of concentrations; the freezing point curve thus obtained presents several interesting features.

Method

Preparation of Materials.—Pure anhydrous acetic acid was prepared as described previously.[7] The freezing point of the acid used in this work was from 16.55 to 16.60°. The salts were purified by recrystallization and thoroughly dried under suitable conditions; the purity of the silver nitrate and the ammonium nitrate was checked by analysis.

Determination of Solubility.—In the case of the silver, sodium and ammonium salts, the synthetic or freezing point method was used;[8] the determinations were carried out in large stoppered test-tubes provided with thermometer and stirrer as previously described. The thermometers were carefully calibrated before use, and each saturation temperature was determined at least twice. The measurements for sodium and silver nitrate were not continued beyond 100°, because of the inconveniently high vapor pressure of acetic acid at higher temperatures; ammonium nitrate, however, was so much more soluble at 100° that the vapor pressure was lowered sufficiently for the determinations to be continued up to the melting point, without change of method.

The accuracy of the determinations varies considerably with the rate of change of solubility with temperature. For the sodium and ammonium nitrate solutions, the equilibrium temperatures reported are believed to be correct to within 0.5°, a considerable portion of the ammonium nitrate data being more accurate than this. In the case of silver nitrate, a very faint turbidity, which persisted up to the boiling point, and may have been brought about by a slight solvolysis, was observed in all the solutions. Because of this fact, together with the extreme steepness of the freezing point curve, the equilibrium temperatures are less accurate; they are believed to be correct to within 1°.

The solubility of the barium nitrate proved to be so small that it could not be determined by the synthetic method. Instead, the concentration of solute in a solution saturated at a fixed temperature was determined by analysis. An excess of the salt was heated with 100 cc. of acid to 100° for forty-five minutes in a stoppered flask. The mixture was then cooled to room temperature, placed in a thermostat and allowed to remain at 30° for two days, with frequent stirring. The concentration of the solution was then determined by precipitation of the barium as sulfate. Because of the extremely small solubility, no high degree of accuracy is claimed for the result; it is correct to within 10%.

Analysis of Solid Phases.—Samples of the solid phases present at equilibrium were obtained by filtration, followed by rapid drying between porous tiles. The products so obtained were then analyzed to determine whether or not acetic acid of solvation was present In the case of the silver nitrate solution, the solid was analyzed both for its silver content, by precipitation as chloride, and for acidity, by titration with sodium hydroxide solution; a rough colorimetric determination of nitrate, by means of phenoldisulfonic acid, was made also. The sodium nitrate was tested merely by titration

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(6) Davidson, THIS JOURNAL, **50**, 1890 (1928).

(7) Ref. 4a, p. 508.

(8) A detailed discussion of the factors affecting the accuracy of this method has been given in a recent article by Sunier, *J. Phys. Chem.*, **34**, 2582 (1930).

for acidity. In the case of the ammonium nitrate, the ammonia was determined by addition of excess of sodium hydroxide solution, followed by distillation into standard hydrochloric acid.

Results

The data obtained are tabulated below, and are represented also in the accompanying diagrams. Concentrations are expressed throughout in mole percentage of solute; T denotes the equilibrium temperature in °C.

I. SILVER NITRATE–ACETIC ACID

Solid phase silver nitrate

$AgNO_3$, %	0.0274	0.0398	0.0439	0.0708
T	30	36	40	54
$AgNO_3$, %	0.1035	0.1332	0.1361	0.1940
T	64	78	81	93

The solubility curve is shown in Fig. 1. The solid phase showed no measurable acidity; analysis for silver gave 62.30% (calcd. for $AgNO_3$, 63.49%). It is evident that the compound is unsolvated silver nitrate.

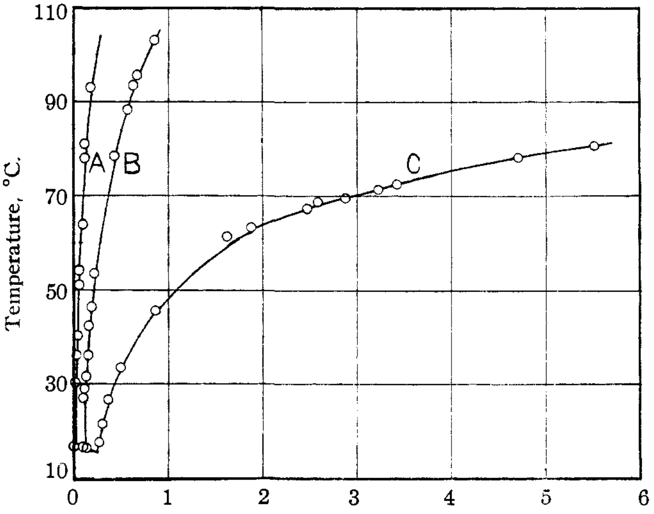

Fig. 1.—Solubility curves for $AgNO_3$ (A), $NaNO_3$ (B) and NH_4NO_3 (C) in anhydrous acetic acid.

A colorimetric test for nitrate gave results in accord with this conclusion. It has been reported[9] that when silver nitrate was treated with an excess of boiling acetic acid, colorless needles of a substance having the formula $(C_2H_3O_2)_2NOH(OAg)_2$ separated on cooling. This formula might equally well be written $Ag_2(C_2H_3O_2)NO_3.HC_2H_3O_2$, and the compound might be regarded as a solvated product of partial solvolysis (a basic salt of the acetic

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[9] Pictet and Klein, *Arch. sci. phys. nat. Genève*, **15**, 589 (1903); *J. Chem. Soc.*, **84**, 1, 675 (1903).

acid system). No such compound could be isolated, however, in the present work.

II. Sodium Nitrate–Acetic Acid

(a) Solid phase acetic acid

$NaNO_3$, %	0.0	0.031	0.139	0.150
T	16.60	16.53	16.48	16.45

(b) Solid phase sodium nitrate

$NaNO_3$, %	0.122	0.139	0.150	0.166	0.173	0.183	
T	27.0	29.0	31.5	36.0	40.0	42.5	
$NaNO_3$, %	0.202	0.246	0.448	0.573	0.641	0.677	0.854
T	46.5	53.7	78.5	88.3	93.4	95.7	103.0

The solubility curve is shown in Fig. 1. The solid phase (b) showed no appreciable acidity, and is therefore unsolvated sodium nitrate.

III. Ammonium Nitrate–Acetic Acid

(a) Solid phase acetic acid

NH_4NO_3, %	0.0	0.0741	0.1287
T	16.60	16.57	16.47

(b) Solid phase ammonium nitrate

NH_4NO_3, %	0.2832	0.3249	0.3916	0.5143	0.8745	1.634
T	17.7	21.4	27.0	33.6	45.8	61.2
NH_4NO_3, %	1.887	2.468	2.636	3.239	3.447	4.710
T	63.5	67.6	69.0	71.4	72.8	78.3
NH_4NO_3, %	5.508	7.255	8.620	13.68	17.15	19.36
T	80.9	85.7	89.0	97.1	101.0	102.6
NH_4NO_3, %	23.30	27.64	31.25	37.98	43.31	47.56
T	106.3	108.9	110.6	113.1	115.8	117.0
NH_4NO_3, %	51.67	55.5	60.1	63.1	66.8	71.6
T	118.3	120.0	121.4	122.9	124.8	128.9
NH_4NO_3, %	75.0	78.6	82.3	86.3	89.6	100.0
T	131.4	136.9	143.1	149.7	157.8	167.5

A small portion of the solubility curve is shown in Fig. 1, and the entire curve, on a smaller scale, in Fig. 2. Analysis of the solid phase (b) in equilibrium with solution at about 30° showed 20.00% of ammonia (calcd. for NH_4NO_3, 21.27%); since the upper portion of the curve terminates at the melting point of ammonium nitrate, the solid phase is evidently unsolvated salt throughout the entire range of concentrations.

Since ammonium nitrate is known to exist in four different crystalline modifications, at ordinary pressure, between −18° and its melting point,[10] the solubility curve might have been expected to exhibit sudden changes in slope at the transition temperatures, namely, 32.3, 84.2 and 125.2°; such discontinuities have, in fact, been observed in the solubility curve for this

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(10) The most recent discussion of the polymorphism of ammonium nitrate is given by Hendricks, Posnjak and Kracek, THIS JOURNAL, **54**, 2766 (1932).

salt in water.[11] In the acetic acid curve, however, these discontinuous changes must be much less marked, those at the two lower temperatures not being detectable at all in Fig. 2. A slight "break," however, may be observed at a temperature of 125°, corresponding to the change from the tetragonal (II) to the cubic (I) modification; this change, incidentally, is accompanied by a far greater heat of inversion than any of the others.

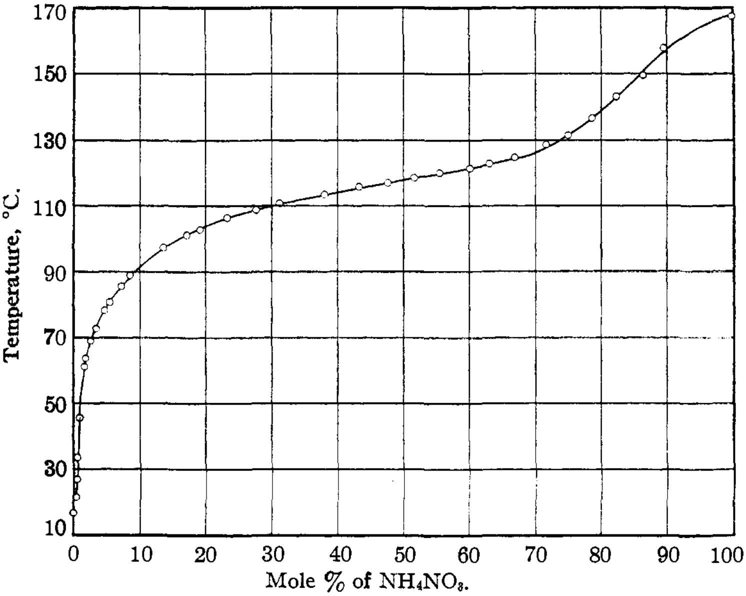

Fig. 2.—System NH_4NO_3–$HC_2H_3O_2$.

The form of the ammonium nitrate–acetic acid curve will be further discussed below.

IV. BARIUM NITRATE–ACETIC ACID

Solid phase $Ba(NO_3)_2$; solubility at 30°, 0.0005%

It was previously reported[12] that this salt was very slightly soluble and could be obtained as a precipitate upon mixing acetic acid solutions of barium iodide and sodium nitrate.

Discussion

The solubilities at 25° of the four salts here studied, together with that of potassium nitrate,[13] are shown in Table I; their solubilities in water[14] are included for purposes of comparison. In both solvents the solid phase is in every case the unsolvated salt.

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(11) "International Critical Tables," Vol. IV, p. 217.

(12) Ref. 6, p. 1893.

(13) Seward and Hamblet, Ref. 5, p. 558. (In the heading of the second column of Table II, "$KClO_4$" appears, evidently as a typographical error, instead of "KNO_3").

(14) Ref. 11, pp. 217–240.

TABLE I

SOLUBILITY OF UNSOLVATED NITRATES IN ACETIC ACID AND IN WATER AT 25°

Salt	Solubility in acetic acid Mole, %	Moles per 1000 g. solvent	Solubility in water Moles per 1000 g. solvent
$Ba(NO_3)_2$	0.0005	0.00008	0.400
KNO_3	.105	.0175	3.74
$NaNO_3$	.121	.0202	10.80
$AgNO_3$	.020	.0033	14.00
NH_4NO_3	.370	.0619	26.98

The fact that interionic forces are much greater in acetic acid than in water makes the former a poorer "salt solvent."[15] Except for silver nitrate, solubility in acetic acid, in this series of salts, increases in the same order as in water; which, incidentally, corresponds to the order of decreasing melting points.

The discontinuous change in slope of the freezing point curve for ammonium nitrate at 125° has been mentioned above. Even aside from this "break," however, the entire course of the curve—steep in its initial portion, flattening out to a long central section of small slope, and becoming steeper again at a high concentration of salt—is of a decidedly unusual character. It resembles somewhat the curve observed for salicylic acid in water by Alexejew,[16] and that for silver perchlorate in benzene discussed by Hill,[17] each of which shows a point of inflection; but in the ammonium nitrate curve there are two distinct points of inflection, at 60% and at 85% of solute, respectively.

It is often of interest, in the study of solubility data, to plot them in the manner suggested by Hildebrand,[18] using as coördinates log N (where N is the mole fraction of solute) and $1/T$, the reciprocal of the absolute temperature at which solution and solute are in equilibrium. In the ideal case (for a solution obeying Raoult's law at all temperatures and pressures) this method of plotting yields a straight line whose slope is $-L_f/4.58$, where L_f is the molal heat of fusion of the solute.[19] In the case under consideration, since both components are polar to different degrees, and since they doubtless also differ considerably in internal pressure, wide and as yet unpredictable deviations from ideal behavior might be anticipated.[20] Nevertheless, it appeared to be worth while to plot the data, at least for that portion of the curve in the vicinity of the melting point of the solute, in the manner just described.

The molecular state of acetic acid in solution is not definitely known.

(15) *Cf.* Hammett and Dietz, THIS JOURNAL, **52**, 4807 (1930).

(16) Alexejew, *Wied. Ann.*, **28**, 330 (1886).

(17) Hill, THIS JOURNAL, **44**, 1163 (1922).

(18) Hildebrand, "Solubility," Chemical Catalog Co., Inc. New York, 1924, p. 148.

(19) If the heat of fusion varies with the temperature, there is a corresponding deviation from a linear relationship.

(20) Ref. 18, chapters VIII and IX. This system would not fall in the class of "regular" solutions, discussed at length by Hildebrand, THIS JOURNAL, **51**, 66 (1929).

This compound is undoubtedly associated in the liquid state, both alone and in solution in many solvents,[21] and association is considerable in the vapor state also,[22] persisting even to temperatures well above the boiling point.[23] On this account, several writers,[24] in discussing systems containing acetic acid as one component, have considered it as having the formula $(C_2H_4O_2)_2$. While it is probable, in the present instance, that a considerable fraction of the acetic acid is in this form in solutions containing a large proportion of the solvent, at low temperatures, it is doubtful that such association would persist in solutions dilute in acetic acid, or at high temperatures. However, mole fractions have been calculated on the basis both of single and of double molecules (molar weight 120) of acetic acid, for purposes of comparison, and the resulting curves have been plotted in Fig. 3. Each of these curves, it will be noticed, shows a slight "break" at a point corresponding to the transition temperature, 125°.

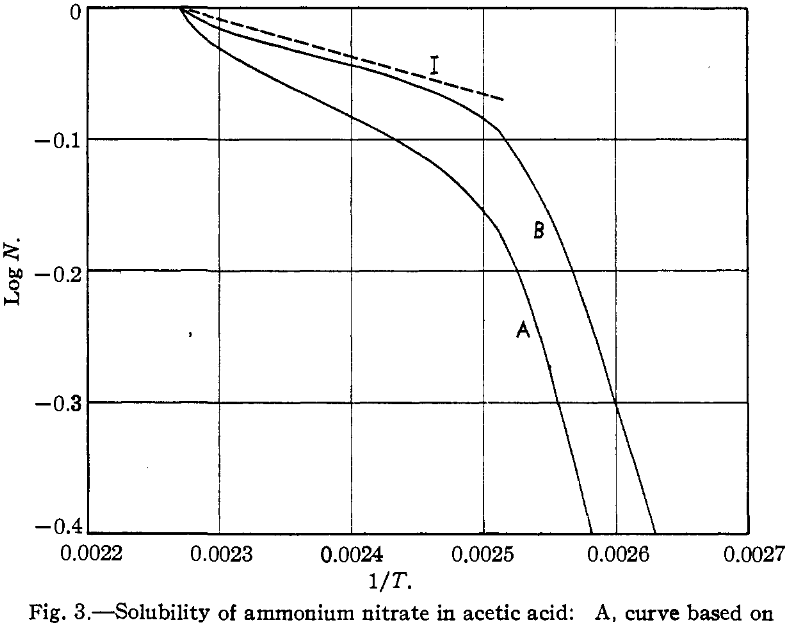

Fig. 3.—Solubility of ammonium nitrate in acetic acid: A, curve based on usual formula for acetic acid; B, curve based on formula $(C_2H_4O_2)_2$; I, approximate course of ideal curve.

The heat of fusion of ammonium nitrate has apparently never been determined by direct calorimetric measurement. However, Bridgman,[25]

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(21) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., Inc., New York, 1931, pp. 173–174.

(22) Drucker and Ullmann, *Z. physik. Chem.*, **74**, 604 (1910).

(23) Trautz and Moschel, *Z. anorg. allgem. Chem.*, **155**, 13 (1926).

(24) Ward, *J. Phys. Chem.*, **30**, 1316 (1926); Roozeboom, "Heterogene Gleichgewichte," Brunswick, 1904, Vol. II, part 1, p. 260.

(25) Bridgman, *Proc. Am. Acad. Sci.*, **51**, 581 (1916).

in a study of the effect of pressure upon the polymorphism of this substance, calculated the heat of fusion, by means of the Clapeyron equation, from the rate of change of melting point with pressure, obtaining the value 6.9 kilogram-meters per gram, which is equivalent to the remarkably low value of 1300 calories per gram mole. Due to the difficulty in determining the increase in volume accompanying fusion, this value is probably not very accurate. In such an approximation, the unknown difference in heat capacity between the solid and liquid forms may be neglected, and the heat of fusion may be regarded as constant over a short temperature range.[26] Using the value of 1300 for L_f, we get -284 as the slope of the ideal curve between the melting point and 125°. This is represented in Fig. 3 by the broken line, the equation for which is $\log N = 0.644 - 284/T$.

It is evident that the experimental curve plotted on the basis of the usual formula for acetic acid deviates very widely from the ideal, even at low concentrations of acid, in the direction of smaller solubility. On the other hand, the curve plotted on the basis of double molecules of acetic acid approaches the ideal position rather closely at temperatures within 35° of the melting point; it is nearly linear over most of this range and has, in fact, practically the slope calculated from the approximate heat of fusion found by Bridgman. In the present state of our knowledge of this system, however, this approach to the ideal curve must be regarded as hardly more than fortuitous.[27] At lower temperatures the solubility appears to fall far below the ideal value; solvation presumably occurs only to a slight extent, if at all.

Summary

1. Quantitative solubility data have been obtained for ammonium, sodium and silver nitrates in acetic acid over a wide range of temperatures, and for barium nitrate at 30°. The solubility of these salts decreases in the order named. No solvates were isolated from any of the solutions.

2. A "break" occurs in the solubility curve of ammonium nitrate at 125°, due to the change in crystalline form which occurs at this temperature.

3. A plot of the logarithm of the mole fraction of ammonium nitrate against the reciprocal of the absolute temperature of equilibrium shows that the solution deviates widely from Raoult's law, as would be expected from the character of the components.

LAWRENCE, KANSAS

RECEIVED AUGUST 22, 1932
PUBLISHED FEBRUARY 9, 1933

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(26) A further complication arises from the probable ionization of the ammonium nitrate, which, if complete, would result in a linear relationship between $\log (2N/(N+1))^2$, instead of $\log N$, and $1/T$ (Ref. 18, p. 165). But the deviation produced by this factor is very small at high concentrations of solute—probably less, in this case, than the uncertainty of the heat of fusion—and has therefore been neglected in locating the ideal curve.

(27) Certainly we should not be justified in concluding that acetic acid was present entirely as double molecules under these conditions. The danger in drawing such conclusions as to the molecular state of substances in solution from the deviation of the solutions from Raoult's law has been repeatedly emphasized by Hildebrand (see, for instance, Ref. 18, pp. 83–84).