Solubilities of Some Uni-Univalent Salts in *N*-Methyl Formamide From 0–35° C.

GEORGIA A. STRACK, SHARON K. SWANDA, and LOWELL W. BAHE
University of Wisconsin-Milwaukee, Milwaukee, Wis.

The solubilities in *N*-methyl formamide (dielectric constant of 182.4 at 25° C.) of NaCl, KCl, NaBr, KBr, NH_4Cl, and NH_4Br were measured over the temperature range 0–35° C. Results for LiCl, NaI, and KI at 25° C. are also reported though side reactions may make the values for these three salts unreliable. The solubilities in *N*-methyl formamide are compared with the solubilities in water, ammonia, formamide, and *N*-methyl acetamide. The solubilities depended on specific solvent-solute interactions and were not a simple function of the dielectric constant of the solvent.

IN COMPARISON TO WATER, relatively little work has been done with solutions of electrolytes in solvents with very high dielectric constants, i.e., with solvents whose dielectric constant is greater than that of water. The solubilities of several uni-univalent electrolytes in *N*-methyl formamide have been measured over the temperature range 0-35° C. *N*-methyl formamide has a high dielectric constant, 182.4 at 25° C. (*12*), a convenient liquid range, -3.8 (*12*) to about 185° C. (*9*), and is fairly easily prepared. *N*-methyl formamide was chosen as a solvent because, as far as could be determined, it has the highest dielectric constant at room temperature of any known liquid.

EXPERIMENTAL

Solubilities. An excess of salt and 10 ml. of NMF in a carefully stoppered 8 inch test tube were placed in a constant temperature bath for 2 to 4 days. The test tubes were shaken manually several times each day. Saturation was assumed when samples taken at least one day apart gave identical concentrations. The solubilities were measured at 0°, 10°, 15°, 20°, 25°, 30°, and 35° C. The temperature was held constant to within 0.01° C. and the absolute temperatures were believed to be reliable to within 0.1° C. Five ml. samples were withdrawn with a pipet equipped with a removable glass wool filter over the tip and transferred to a glass-stoppered weighing bottle. The weighed contents of the weighing bottle were diluted to 100 ml. with water and the halide titrated by Fajan's method. To check the reliability of the method, known samples of halide salts mixed with *N*-methyl formamide in water were analyzed with excellent results. Berger and Dawson (*2*) found similar results when analyzing halides in the presence of formamide by Fajan's method.

The density of each solution was found by dividing the weight of the sample by the volume of the pipet used in taking the sample. Since the temperature of the solution in the pipet was probably somewhat different from the temperature of the solution in the constant temperature bath, these densities are not as accurate as the corresponding weight data. The densities were used to calculate concentrations on a molarity scale; we estimate the results are accurate to 2% on the molarity scale, and to 1% on the molality and mole ratio scales.

***N*-methyl Formamide.** NMF was prepared by either of two methods: the addition of methyl amine to formic acid (*12*) or by the classical method of the addition of methyl amine to ethyl formate (*2*). Yields were 80% or more based on the acid or the ester. The water or alcohol was stripped off by simple distillation and the crude NMF distilled at one to 10 mm. of Hg pressure. Distillation at higher temperatures resulted in considerable decomposition. The NMF was then fractionally recrystallized until the conductance reached a value of between 10^{-3} and 10^{-4} ohm^{-1} $cm.^{-1}$ Recrystallizing to smaller conductances proved wasteful since NMF stored in tightly-stoppered brown glass bottles at room temperatures showed a spontaneous increase of conductance with time that leveled off (at least the change became very slow) between 10^{-3} and 10^{-4} ohm^{-1} $cm.^{-1}$ The NMF showed a strong tendency to supercool and the original crystals could only be obtained at dry ice temperatures. Once seed crystals were available, however, crystallization at any temperature below the melting point went smoothly. The spontaneous increase of conductance with time and the strong tendency to supercool have been noted previously (*5*).

The physical constants of our NMF were (literature values in parentheses): n^{25}_{D} = 1.4305 [1.4300 (*3*), 1.4310 (*12*)]; ρ^{21}_{4} = 1.01 [1.008 at 15° C. (*5*)]; B.P. = 62 at 6 mm. of Hg [51 at 1 mm. of Hg (*5*)].

Salts. Anhydrous, analytical reagent grade salts were used without further purification after drying at 105° C. for 24 hours. In all cases, salts and solvent were stored and transferred in such a manner as to minimize the absorption of atmospheric moisture.

Analysis of the Solid Phase. The equilibrium state of the solid phase in solubility studies may not be the unsolvated salt. After equilibrium had been attained, a sample of the solid phase was blotted as well as possible with paper towels and a weighed sample analyzed for purity by titrating using the same method as that used in determining the concentration of the liquid phase.

RESULTS

The solubilities of the nine salts used in this study are shown in Table I at 25° C. For comparison purposes, the solubilities of these salts in water (*10*), ammonia (*14*), and formamide (FA) (*6*) at 25° C. and in *N*-methyl acetamide (NMA) (*4*) at 40° C. are also listed. The density data necessary to change the data in NMA to a mole ratio were not reported, so the results are shown in terms of the molarity scale of concentration.

The solubilities of LiCl, NaI, and KI in NMF are enclosed in parentheses to indicate doubt about the values. As soon as LiCl came in contact with NMF, heat was liberated and the original free-flowing crystals formed a solid mass. Analysis of the solid phase showed a strong likelihood of some degree of solvation, though the degree of solvation could not be determined. Also, equilibrium had not been attained at the end of three weeks at 25° C. The value reported here is the maximum obtained. The concentrated solution obtained showed a high viscosity compared to the original solvent.

The liquid phases over both NaI and KI showed a slight brownish-yellow tinge after 24 hours at 25° C., and the color became darker after standing for longer periods of time. A starch test indicated the presence of free iodine. Bubbling nitrogen through the solvent to remove dissolved oxygen before placing in contact with the iodides, and keeping the systems under a blanket of nitrogen did not eliminate the appearance of this color. Iodide is apparently spontaneously oxidized to iodine to some extent in NMF at these high concentrations. The values reported here are those obtained with the amount of free iodine formed in four days.

The analysis of the solid phases for each salt except LiCl indicated no solvation of the salt in the solid phase. The solids remained free-flowing in all cases except, again, LiCl.

Because of the difficulties encountered with LiCl, NaI, and KI, these salts were not included in the solubilities measured at other temperatures. Within the limits of accuracy, the solubilities in molal units were found to be linear functions of temperature over the temperature range 0–35° C. The constants *A* and *B* in the equation:

$$m_{ss} = AT + B \tag{1}$$

were found for each salt by the method of least squares. In this equation, m_{ss} is the molality of the saturated solution, *T* is the absolute temperature, and *A* and *B* are constants. Values for *A* and *B* for the six salts measured are listed in columns 2 and 3 of Table II.

Table I. Solubilities at 25° C. in *N*-methyl formamide (NMF) (this work), water (*10*), ammonia (*14*), and formamide (FA) (*6*), and at 40° C. in *N*-methyl acetamide (NMA) (*4*).

Salt	Solvent	Molarity	Moles/100 Moles Solvent
NaCl	NMF	0.544	3.25
	H_2O		11.10
	NH_3		0.879
	NMA	0.339	
	FA		7.18
KCl	NMF	0.273	1.62
	H_2O		8.67
	NH_3		0.0092
	NMA	0.120	
	FA		3.81
NaBr	NMF	2.56	16.4
	H_2O		16.4
	NH_3		22.8
	NMA	1.850	
	FA		15.69
KBr	NMF	0.812	4.94
	H_2O		10.2
	NH_3		1.93
	NMA	0.429	
	FA		8.09
NH_4Cl	NMF	0.906	5.56
	H_2O		13.29
	NH_3		32.57
	NMA	0.896	
	FA		9.28
NH_4Br	NMF	2.20	14.3
	H_2O		13.9
	NH_3		41.3
	NMA	1.745	
	FA		16.59
LiCl	NMF	(5.05)	(33.7)
	H_2O		35.0
	NMA	0.413	
	FA		
NaI	NMF	(4.25)	(30.7)
	H_2O		22.23
	NH_3		18.4
	NMA	2.86	
	FA		17.01
KI	NMF	(2.57)	(17.3)
	H_2O		15.5
	NH_3		18.6
	NMA	1.356	
	FA		18.78

The densities of the saturated solutions over the temperature range 0–35° C. were constant for all the salts tested except for NaBr in which case the density was a linear function of temperature. The densities are given in column 4 of Table II.

DISCUSSION

If the dielectric constant were the only property, or even the property of overwhelming importance, that determined the solubility of electrolytes, we might expect the solubilities to lie in the order of the dielectric constants. The dielectric constants (given at 25° C.) of the solvents listed in Table I lie in the order NMF, 182.4 (*12*), = NMA, 175.7 at 30.5° C. (*12*), > FA, 109.5 (*11*), > H_2O, 78.54 (*16*), > NH_3, 16.9 (7). The solubilities in Table I do not lie in the order of the dielectric constants. Furthermore, if the dielectric constant were the only important consideration, then the solubilities of every uni-univalent salt in a particular solvent ought to be very similar (if each salt is completely dissociated in solution). A wide variation is found as Table I shows. These data indicate that the solubilities are quite specific in nature and must depend upon quite specific interactions between solvent and solute.

The difference between the partial molar enthalpy of the salt at infinite dilution and the partial molar enthalpy of the salt in the pure state is given by (*15*):

$$H^{*} - H^{\Delta} = \nu RT^{2}(\partial \ln m^{\pm}/\partial T + \partial \ln \gamma^{\pm}/\partial T) \tag{2}$$

The determination of the enthalpy difference should be possible from our data if the rate of change of the logarithm of the activity coefficient could be evaluated. To a first approximation, we assumed that the rate of change of the logarithm of the activity coefficient with temperature was small enough to ignore. Some indication of the severity of this assumption could be made from the Debye-Huckel theory if more information were available for this solvent system. A very crude estimate indicates that the rate of change of the second term on the right of Equation 2 is of the same order of magnitude as the first term, so the assumption may be very poor (*8*). In the last column of Table II we give the heat of solution calculated from Equation 2 if the second term on the right is ignored. This is the heat attending the dissolution of one mole of pure salt in enough NMF to form an infinitely dilute solution at 25° C., given our assumption. These heats are all very small, just as they are small for water.

Table II. Data for Solutions of Salts in *N*-methyl formamide

A and *B* are the constants in Equation 1. ρ is the density of the saturated solutions. $H^{*} - H^{\Delta}$ is the heat of solution to form an infinitely dilute solution assuming that the activity coefficient does not vary with temperature.

Salt	*A*	*B*	ρ, G./Ml.	$H^{*} - H^{\Delta}_{298}$, Kcal./Mole
NaCl	−0.001868	1.0984	1.02	−1.197
NaBr	−0.012075	6.4708	1.21[a]	−1.539
KCl	0.0	0.273	1.01	0.0
KBr	−0.001022	1.1586	1.06	−0.431
NH_4Cl	0.003785	−0.1827	1.01	1.422
NH_4Br	0.0	2.45	1.11	0.0

[a] The densities were all independent of temperature except for NaBr which was linear with temperature. The value in the table refers to 0° C. and the value at 35° C. was 1.17 g./ml.

A similar analysis of the data given by Gopal and Husain (*6*) for the solubility of these six salts in formamide has been carried out. The constants in Equation 1 were determined by the method of least squares and the heat of solution at 25° C. determined in the same way as that used above for *N*-methyl formamide solutions. The results are shown in Table III. Again it can be seen that the heats of solution are very small. It must be pointed out, however, that there is not good agreement between the results calculated here and those obtained by a direct calorimetric method by Mishchenko and Sukhotim (*13*) in formamide in those cases where comparison is possible. However, this lack of agreement may result from our assumption that the activity coefficient does not change with temperature. The results in both cases indicate that the heats of solution are quite small.

Table III. Constants in Equation 1 for the Solubilities as a Function of Temperature for Salts in Formamide

Calculated from data given by Gopal and Husain (*6*). Heats of solution were calculated from the solubility data assuming that the activity coefficient does not vary with temperature.

Salt	A	B	$m_{ss_{\text{calcd.}}}^{(298)}$	$H^* - H^{\Delta}_{298}$, Kcal./Mole
NaCl	−0.006074	3.3968	1.586	−1.354
NaBr	0.03095	−5.7337	3.496	3.129
KCl	0.002057	0.2279	0.841	0.864
KBr	0.002606	1.0244	1.802	0.511
NH_4Cl	0.01306	−1.8334	2.061	2.240
NH_4Br	0.01714	−1.4253	3.686	1.644

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Vapor Pressure of Liquid Methanol at Low Temperatures

GEORGE A. MILLER
Georgia Institute of Technology, Atlanta, Ga.

The vapor pressure of liquid CH_3OH was measured near the melting point. The results were used in a third law calculation to test the consistency of various thermodynamic data for the liquid and vapor. The most apparent uncertainty lies in the equation of state of the vapor.

FROM X-RAY diffraction studies of crystalline methanol at low temperatures (*11, 18*) it is known that there is no residual entropy from random hydrogen bonding such as occurs in the related case of ice. However, the spectroscopic entropy value was not brought into reasonable agreement with the calorimetric value until it was first shown that methanol vapor is exceedingly nonideal (*19*). Even then the problem was compounded by the presence of a transition in the solid inconveniently close to the melting point, by some remaining uncertainty in the value of the barrier to internal rotation, and by the fact that not all of the normal frequencies could be identified from the vibrational spectrum. Recent work has surmounted these difficulties. Thus, the heat capacity of the solid and liquid has been remeasured with considerable care (*2*), the barrier to internal rotation is accurately known from the microwave spectrum (*7*), and the vibrational assignment has been all but settled through normal coordinate analyses (*3, 12, 20*).