[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

An Interpretation of the Acidity Function in Glacial Acetic Acid

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The "acidity function" in dilute glacial acetic acid solutions is a linear function of the logarithm of the equilibrium concentration of undissociated acid present. Expressions are derived relating the apparent acidity function in glacial acetic acid to thermodynamic equilibrium constants in water and glacial acetic acid for a solution of a pure acid or salt, a mixture of an acid and its salt, and a mixture of a base and its salt. It is demonstrated that the acidity function in acetic acid depends upon the choice of reference indicator base. The effect of small concentrations of water on the acidity function in acetic acid is quantitatively explained in terms of the reaction $H_2O + HX \rightleftarrows H_3O^+X^-$.

The acidity function H_0 was defined originally by Hammett[1] as

$$H_0 = -\log (K_{\mathrm{HB^+}})_{\mathrm{w}} + \log \frac{[\mathrm{B}]}{[\mathrm{HB^+}]} = -\log [\mathrm{H^+}] f_{\mathrm{H^+}} f_{\mathrm{B}}/f_{\mathrm{HB^+}} \qquad (1)$$

where $(K_{\mathrm{HB^+}})_{\mathrm{w}}$ is the thermodynamic dissociation constant in water for the reaction

$$\mathrm{HB^+} \rightleftarrows \mathrm{H^+} + \mathrm{B} \qquad (2)$$

If the cation acid HB^+ and/or its uncharged conjugate base B is colored, it is possible to determine the ratio $[B]/[BH^+]$ spectrophotometrically. H_0 then can be calculated for the solution in question from eq. 1, provided $(K_{\mathrm{HB^+}})_{\mathrm{w}}$ is known. Values for $(K_{\mathrm{HB^+}})_{\mathrm{w}}$ are given by Paul and Long.[2]

Acidity functions have been determined for various solvent–acid mixtures, and it is found that H_0 is usually independent of the reference indicator base used in high dielectric constant solvents. The theoretical basis of this result in high dielectric constant solvents is discussed by Paul and Long.[3] However, in a low dielectric constant solvent like glacial acetic acid, H_0 depends on the reference indicator base chosen. Various authors[4-9] have criticized the extension of the H_0 function to media of low dielectric constant. Expressions are derived below which relate the apparent acidity function in acetic acid $(H_0)_{\mathrm{app.}}$ with thermodynamic equilibrium constants in water and acetic acid.

Discussion

In a low dielectric constant solvent, such as acetic acid, the ion pair dissociation constant of an indicator salt IH^+X^- is very small and usually less than 10^{-5}.[10] Thus the dissociation reaction

$$\mathrm{IH^+X^-} \rightleftarrows \mathrm{IH^+} + \mathrm{X^-} \qquad (3)$$

does not proceed significantly to the right in the presence of appreciable concentrations of the acid HX. The relatively large concentration of X^- ion produced by the dissociation of the acid HX represses the dissociation of IH^+X^-. Therefore, the reaction governing the color equilibrium of an indicator and an acid in acetic acid is

$$\underset{\text{basic color}}{\mathrm{I} + \mathrm{HX}} \rightleftarrows \underset{\text{acid color}}{\mathrm{IH^+X^-}} \qquad (4)$$

not, as in water

$$\underset{\text{basic color}}{\mathrm{I} + \mathrm{H^+}} \rightleftarrows \underset{\text{acid color}}{\mathrm{IH^+}} \qquad (5)$$

It is not possible to distinguish between reactions 4 and 5 on the basis of a plot of log [Acid Color]/[Basic Color] *vs.* log [Analytical Concn. of Acid]. Both give a straight line of slope one for such a plot if the concentration of indicator is much smaller than the concentration of acid. It is possible to relate $(H_0)_{\mathrm{app.}}$ in glacial acetic acid to thermodynamic dissociation constants in both water and glacial acetic acid, providing the incomplete dissociation of all species present in the glacial acetic acid is taken into account.

The equilibrium constant for reaction 4 is

$$K_f^{\mathrm{IHX}} = \frac{[\mathrm{IH^+X^-}]}{[\mathrm{I}]\,C_{\mathrm{HX}}} \qquad (6)$$

(The notation employed in the following material is the same as that used in reference 11. Note that $C_{\mathrm{HX}} = [\mathrm{HX}] + [\mathrm{H^+X^-}]$.) Thus

$$-\log C_{\mathrm{HX}} = \log K_f^{\mathrm{IHX}} + \log [\mathrm{I}]/[\mathrm{IH^+X^-}] \qquad (7)$$

or

$$-\log C_{\mathrm{HX}} = \log K_f^{\mathrm{IHX}} + \log [\text{Basic Color}]/[\text{Acid Color}] \qquad (8)$$

The apparent acidity function $(H_0)_{\mathrm{app.}}$ in glacial acetic acid is written conventionally

$$(H_0)_{\mathrm{app.}} = (pK_{\mathrm{IH^+}})_{\mathrm{w}} + \log [\text{Basic Color}]/[\text{Acid Color}] \qquad (9)$$

where $(pK_{\mathrm{IH^+}})_{\mathrm{w}}$ is the negative logarithm thermodynamic dissociation constant for the reverse of reaction 5 in water. Elimination of the logarithmic term involving the ratio of colored indicator species between equations 8 and 9 yields

$$(H_0)_{\mathrm{app.}} = (pK_{\mathrm{IH^+}})_{\mathrm{w}} - \log K_f^{\mathrm{IHX}} - \log C_{\mathrm{HX}} \qquad (10)$$

Equation 10 is applicable to acetic acid solutions containing only pure acid, HX, a solution containing HX and its salt BHX, a solution containing only BHX, and a solution containing a base B and the salt BHX.

Solutions Containing Only HX.—In a glacial acetic acid solution of an acid HX eq. 10 predicts that $(H^0)_{\mathrm{app.}}$ will be linear with the logarithm of the equilibrium concentration of undissociated acid. In most practical cases, the stoichiometric

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[1] L. P. Hammett, *Chem. Revs.*, **16**, 67 (1935).

[2] M. A. Paul and F. A. Long, *ibid.*, **57**, 1 (1957).

[3] F. A. Long and M. A. Paul, *ibid.*, **57**, 935 (1957).

[4] J. Rojek, *Collection Czechoslov. Chem. Communs.*, **22**, 1 (1957).

[5] D. P. B. Satchell, *J. Chem. Soc.*, 1916 (1958).

[6] R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, **38**, 699 (1955).

[7] D. S. Noyce and W. A. Pryor, THIS JOURNAL, **77**, 1397 (1955).

[8] (a) E. Grunwald and B. J. Berkowitz, *ibid.*, **73**, 4939 (1951); (b) B. Gutbezahl and E. Grunwald, *ibid.*, **75**, 559 (1953); (c) *ibid.*, **75**, 565 (1953).

[9] J. N. Brønsted, *Z. physik. Chem.*, **169**, 52 (1934).

[10] I. M. Kolthoff and S. Bruckenstein, THIS JOURNAL, **78**, 1 (1956).

[11] S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2974 (1956).

concentration of acid and the equilibrium concentration of undissociated acid are virtually the same, so that a plot of $(H_0)_{\text{app.}}$ *vs.* the logarithm of the analytical concentration of acid will be a straight line of slope minus one. This has been found to be the case for perchloric acid, sulfuric acid (which is a weak monobasic acid in glacial acetic acid), hydrochloric acid, and seven other acids in dilute (less than 0.01 *M*) solution.[12] Hall and Spengeman[13] studied sulfuric acid solutions in acetic acid and found $(H_0)_{\text{app.}}$ to be linear with $-\log C_{\text{H}_2\text{SO}_4}$ below 0.01 *M* acid but that deviations occurred at high concentrations of sulfuric acid. Ultimately $(H_0)_{\text{app.}}$ becomes linear with stoichiometric concentration of acid. This behavior is similar to that observed in aqueous solutions and, as in water, the simple logarithmic correlation between $(H_0)_{\text{app.}}$ and species in solution is restricted to dilute solution.

If, instead of choosing the indicator I as the reference base, the indicator I′ had been chosen, the difference between the apparent acidity functions, $\Delta_{\text{I,I}'}(H_0)_{\text{app.}}$, obtained using I and I′ in the same HX solution in acetic acid, would be

$$\Delta_{\text{I,I}'}(H_0)_{\text{app.}} = (pK_{\text{IH}^+})_{\text{w}} - (pK_{\text{I}'\text{H}^+})_{\text{w}} - \log K_{\text{f}}^{\text{IHX}}/K_{\text{f}}^{\text{I}'\text{HX}} \quad (11)$$

In general, the difference in acidity functions is not zero. Hall and Spengeman's data yield $\Delta_{\text{I,I}'}(H_0)_{\text{app.}} = -0.41$ when I = *o*-nitraniline, I′ = 2,4-dichloro-6-nitroaniline and HX = sulfuric acid. Deviations of similar magnitude were found by Roček[4] for perchloric acid in acetic acid containing 10% water and for phosphoric acid in acetic acid containing 1% water.

In view of the fundamental difference between the equilibria governing the color of indicators in water and acetic acid, it is somewhat surprising at first glance that larger differences are not found between acidity function values obtained using different reference bases. However, more careful considerations lead to conclusions in agreement with the experimental results.

It can be shown[11] that $K_{\text{f}}^{\text{IHX}} = K_{\text{HX}}/K_{\text{IH}^+} \cdot K_{\text{IHX}}$, where K_{HX} is the over-all dissociation constant of HX, K_{IH^+} is the dissociation constant of IH$^+$, and K_{IHX} is the dissociation constant of IHX in acetic acid. Thus, eq. 11 becomes

$$\Delta_{\text{I,I}'}(H_0)_{\text{app.}} = \log \frac{(K_{\text{I}'\text{H}^+})_{\text{w}} K_{\text{IH}^+} K_{\text{IHX}}}{(K_{\text{IH}^+})_{\text{w}} K_{\text{I}'\text{H}^+} K_{\text{I}'\text{HX}}} \quad (12)$$

One would not expect the ratio of the indicator acid strengths in water, $(K_{\text{I}'\text{H}^+})_{\text{w}}/(K_{\text{IH}^+})_{\text{w}}$, to be very different from the ratio of the indicator acid strengths in glacial acetic acid, $K_{\text{I}'\text{H}^+}/K_{\text{IH}^+}$. The dissociation constants of the indicator salts in acetic acid, $K_{\text{I}'\text{HX}}/K_{\text{IHX}}$, may reasonably be expected to be within an order of magnitude of each other.[14] Thus, $\Delta_{\text{I,I}'}(H_0)_{\text{app.}}$ might be expected to be as large as one unit in an extreme case. Extreme differences in $(H_0)_{\text{app.}}$ would not be expected when indicators of very similar chemical nature and size are compared.

In dilute aqueous solution there is no significant difference in H_0 values found for dilute solutions of strong acids. However, in acetic acid as a solvent, even if the same indicator is used as reference base, there are extremely large differences in $(H_0)_{\text{app.}}$ found at the identical concentration of acids such as perchloric, hydrochloric and sulfuric. This results from the very weak basic character of acetic acid. The data of Lemaire and Lucas[15] show that the apparent acidity functions of equal concentrations of perchloric and sulfuric acids differ by -1.33 unit (using the same reference indicator). Smith and Elliot[12] report -1.18 and -1.99 for the differences in apparent acidity function of perchloric acid and sulfuric acid and perchloric acid and hydrochloric acid, respectively. If the difference in apparent acidity functions is obtained for two acid solutions containing equal concentrations of HX and HX′ separately, using the same reference indicator, and is written as $\Delta_{\text{HX,HX}'}(H_0)_{\text{app.}}$, it follows from eq. 10 that

$$\Delta_{\text{HX.HX}'}(H_0)_{\text{app.}} = \log K_{\text{f}}^{\text{IHX}'}/K_{\text{f}}^{\text{IHX}} \quad (13)$$

The formation constants in eq. 13 may be written in terms of the relevant over-all dissociation constants[11] yielding

$$\Delta_{\text{HX.HX}'}(H_0)_{\text{app.}} = \log K_{\text{HX}'}K_{\text{IHX}}/K_{\text{HX}}K_{\text{IHX}'} \quad (14)$$

This difference in apparent acidity functions will ordinarily differ from zero. The difference will follow qualitatively the difference in pK values of HX and HX′ but will not be equal to $pK_{\text{HX}} - pK_{\text{HX}'}$ since the dissociation constants of the indicator ion pairs will be sensitive to the size of the anion. The actual differences in the pK values of perchloric and sulfuric acid and perchloric and hydrochloric acid are -2.37 and -3.68, respectively,[11] as compared to respective differences of acidity functions of -1.2 and -2.0.[12] Equation 14 also shows that the difference in the acid strength of two acids cannot be determined by measuring the apparent acidity function of the same concentration of two difference acids, a procedure suggested by Smith and Elliot.[12]

Solutions Containing HX and BHX.—The effect of adding a salt BHX to a solution of an acid HX upon the apparent acidity function is determined by the equilibrium

$$\text{BHX} \rightleftharpoons \text{HX} + \text{B} \quad (15)$$

If the equilibrium concentration of acid is unchanged by addition of the salt, there is no change in $(H_0)_{\text{app.}}$ and all the conclusions of the previous section apply. Ordinarily, the addition of salt will have a negligible effect on the equilibrium concentration of acid; *e.g.*, Smith and Elliot[12] report that the addition of 0.01 *M* sodium perchlorate to perchloric acid solutions (10^{-3} for 10^{-2} *M*) alters $(H_0)_{\text{app.}}$ negligibly. Similarly, the addition of 0.027 *M* NaHSO$_4$ to a 0.027 *M* sulfuric acid solution produces only a change of -0.04 in $(H_0)_{\text{app.}}$.[16] (No consideration is given to the possibility of forming ionic aggregates containing the IH$^+$ ion. This is a distinct possibility at high

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[12] T. L. Smith and J. H. Elliot, THIS JOURNAL, **75**, 3566 (1953).

[13] N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2483 (1940).

[14] It has been found[11] that the dissociation constants of sodium, potassium and lithium chlorides and urea hydrochlorides are within an order of magnitude of each other, as are the dissociation constants of sodium and diethylanilinium perchlorates.

[15] H. Lemaire and H. J. Lucas, THIS JOURNAL, **73**, 5198 (1951).

[16] M. A. Paul and L. P. Hammett, *ibid.*, **58**, 2182 (1936)

salt concentrations and can lead to erroneous values of $(H_0)_{\text{app.}}$; *e.g.*, the addition of 0.0797 *M* $NaHSO_4$ to 0.027 *M* H_2SO_4 decreases $(H_0)_{\text{app.}}$ by 0.23.[16])

If the analytical concentration of acid is extremely low or the formation constant for BHX is very small, the equilibrium concentration of acid, HX, may be calculated as has been described previously[17] and eq. 10 used to calculate the change in $(H_0)_{\text{app.}}$

Solutions Containing BHX and B.—The color of an indicator in acetic acid solution of a base B and a salt of the base BHX is determined by the equilibrium concentration of acid, arising from the reaction

$$\mathrm{B} + \mathrm{HX} \rightleftarrows \mathrm{BHX} \qquad (16)$$

If the equilibrium constant for reaction 16, $K_f^{\text{BHX}} = C_{\text{BHX}}/C_{\text{B}}C_{\text{HX}}$, is combined with eq. 10, the apparent acidity function of a solution of a base and a salt of the base is

$$(H_0)_{\text{app.}} = (pK_{\text{IH}^+})_{\text{w}} + \log K_f^{\text{BHX}}/K_f^{\text{IHX}} - \log C_{\text{BHX}}/C_{\text{B}} \qquad (17)$$

Under many conditions[17] it is a good approximation to assume that the ratio of the equilibrium concentration of salt to base is the same as the ratio of the analytical concentrations. For example, Hall and Meyer[18] found that a plot of $(H_0)_{\text{app.}}$ *vs.* $\log C_{\text{B}}/C_{\text{BHX}}$ were straight lines of slope 1.05 for urea and 0.83 for antipyrine, where HX is sulfuric acid.

The difference in the apparent acidity functions obtained with two different reference indicators in the same mixture of base and salt is given by eq. 11, the same result being obtained in a solution containing only an acid.

The difference of apparent acidity functions obtained using the same reference indicator in a solution of B and HX and B and HX′ when $C_{\text{B}}/C_{\text{BHX}} = C_{\text{B}}/C_{\text{BHX}'}$ is

$$\Delta_{\text{BHX/B,BHX}'/\text{B}}(H_0)_{\text{app.}} = \log K_{\text{BHX}'}K_{\text{IHX}}/K_{\text{BHX}}K_{\text{IHX}'} \qquad (18)$$

$\Delta_{\text{BHX/B,BHX}'/\text{B}}(H_0)_{\text{app.}}$ is not the same as $\Delta_{\text{HX,HX}'}(H_0)_{\text{app.}}$ (compare eq. 18 with eq. 14). Qualitatively, this difference arises from the fact that the value of K_{HX} depends markedly on the extent of acid–base interaction with the solvent in addition to the ion pair dissociation constant of the acid–solvent reaction product.[10] Thus, the ratio of $K_{\text{HX}'}/K_{\text{HX}}$ decreases very rapidly as HX′ becomes weaker with respect to HX, while the ratio $K_{\text{BHX}'}/K_{\text{BHX}}$ depends primarily on the sizes of the BH^+, X^- and X'^- ions, assuming both BHX and BHX′ are completely ionic.

Hall and Meyer[18] found that $(H_0)_{\text{app.}} = 0.98$ for an equimolar mixture of urea and urea bisulfate, using *o*-nitroaniline as reference. The data of Kolthoff and Bruckenstein[10] and Smith and Elliot[12] can be used to calculate $(H_0)_{\text{app.}}$ of +0.8 and +1.0 for equimolar mixtures of urea and urea perchlorate, and urea and urea hydrochloride, respectively, referred to *o*-nitroaniline. Table I presents the differences in apparent acidity functions observed in solutions of pure acids and solutions of bases and salts, along with the difference in logarithm of the over-all dissociation constants of the acids. It is evident that even when the same reference indicator base is used, the apparent acidity function in acetic acid must be interpreted with care. A comparison of the strong acids in water as a solvent would show only small differences for the analogous quantities listed in Table I.

TABLE I

COMPARISON OF $\Delta(H_0)_{\text{app.}}$ FOR SOME ACIDS WITH ΔpK_{HX}

HX	$\Delta_{\text{HClO}_4,\text{HX}'}(H_0)_{\text{app.}}$	$\Delta_{\frac{\text{BHClO}_4}{\text{B}},\frac{\text{BHX}}{\text{B}}}(H_0)_{\text{app.}}$[a]	$\log K_{\text{HX}}/K_{\text{HClO}_4}$
$HClO_4$	0.00	0.00	0.00
H_2SO_4	−1.20	−0.1	−2.36
HCl	−2.0	−0.2	−3.68

[a] B = urea.

Solutions of Pure Salts.—The apparent acidity function of solutions of pure salts in glacial acetic acid has not been reported previously. Reactions 4 and 15 determine the equilibrium concentration of HX in a mixture of BHX and I. The equilibrium concentration of acid in a solution of BHX and I has been calculated in terms of the formation constants K_f^{IHX} and K_f^{BHX} and the concentration of salt, BHX and the total indicator concentration.[17] The result is a cubic expression in C_{HX} which could be solved explicitly for C_{HX} and substituted into eq. 10. However, the resulting expression is not easily interpreted.

For simplicity, it is assumed that the concentration of indicator is zero, yielding the approximate expression, eq. 19, for the equilibrium concentration of acid

$$C_{\text{HX}} = \sqrt{\frac{C_{\text{BHX}}}{K_f^{\text{BHX}}}} \qquad (19)$$

Substituting eq. 19 into eq. 10, eq. 20 is obtained.

$$(H_0)_{\text{app.}} = (pK_{\text{IH}^+}) + {}^1/_2 \log K_f^{\text{BHX}} - {}^1/_2 \log C_{\text{HX}} \qquad (20)$$

Equation 20 predicts that a plot of $(H_0)_{\text{app.}}$ *vs.* $\log C_{\text{BHX}}$ is a straight line of slope −1/2. Published date[16] on the color of *p*-naphtholbenzein in solutions of sodium perchlorate and diethylanilinium perchlorate are in agreement with the above discussion.

Because of the approximate nature of eq. 20 in salt solutions which contain an indicator, no detailed considerations will be given for the apparent acidity function obtained with two different indicators in the same salt solution or with the same indicator in solutions of different salts. It is evident that the results would be different from the cases considered previously.

Effect of Water.—The effect of water on the apparent H_0 function in glacial acetic acid can be treated quantitatively in terms of the reaction

$$H_2O + HX \rightleftarrows H_3O^+X^- \qquad (21)$$

provided the water concentration is less than about 0.4 *M*. Equation 21 represents the formation of the hydronium salt of the acid, and the equilibrium constant for the reaction as written is $K_f^{\text{H}_3\text{O}^+\text{X}^-}$. Water has a significant effect on the color of an indicator base only in solutions of

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[17] I. M. Kolthoff and S. Bruckenstein, THIS JOURNAL, **79**, 1 (1957).

[18] N. F. Hall and F. Meyer, *ibid.*, **62**, 2493 (1940).

acids and/or their salts.[19] For simplicity only the cases of a solution of a pure acid and an acid and its salt will be discussed. In the latter instance, it will be assumed that reaction 15 contributes negligibly to the equilibrium concentration of acid. In both these examples it is derived easily from eq. 10 and $K_f^{H_3O^+X^-}$ that

$$(H_0)_{app.(w)} = (pK_{1H^+})_w - \log K_f^{1HX} - \log (C_{HX})_t + \log (1 + K_f^{1HX} C_{H_2O}) \quad (22)$$

where $(H_0)_{app.(w)}$ is the apparent acidity function in a solution containing an analytical concentration of acid $(C_{HX})_t$ and an equilibrium concentration of water C_{H_2O}. So long as C_{H_2O} is approximately equal to the analytical concentration of water, a plot of $(H_0)_{app.(w)}$ *vs.* log $(C_{HX})_t$ is a straight line of slope minus one. This line will be displaced from the line obtained in anhydrous acetic acid by the value of term, $\log (1 + K_f^{H_3O^+X^-} C_{H_2O})$.

Ludwig and Adams[20] have determined the apparent acidity function of dilute perchloric acid solutions (C_{HClO_4}, 0.1 M) in acetic acid containing varying amounts of water. They present a figure with H_0 as the ordinate and $-\log C_{HClO_4}$ as abscissa. As predicted by eq. 22 this figure contains a family of parallel straight lines of unit slope. Using a previously determined value of $K_f^{H_3OClO_4} = 34$,[10] it is calculated from eq. 22 that the displacement in the vertical direction between the lines representing anhydrous and acetic acid containing 1.95% water should be 1.6 H_0 unit. The displacement found from the figure of Ludwig and Adams is about 1.7 to 1.8 units. This agreement is excellent considering that these authors used different indicators in obtaining the acidity function data in anhydrous and wet acetic acid. The results obtained with *p*-naphtholbenzein and perchloric acid[10,19] and *o*-nitroaniline and perchloric acid[12] are also in agreement with eq. 22.

Generally, the effect of water is adequately described by reaction 21 if the concentration of water is less than about 0.4 M. At higher concentrations of water the nature of the solvent is changed markedly; specifically the dielectric constant increases. Thus Wiberg and Evans[21] suggest that in the concentration range 3 to 15 M water the hydronium ion apparently is hydrated by one molecule of water because they find that in perchloric acid solutions H_0 is proportional to 2 log C_{H_2O}. We[22] find similar behavior for sulfuric acid solutions starting about 1 M water.

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(19) S. Bruckenstein and I. M. Kolthoff, THIS JOURNAL, **79**, 5915 (1957).

(20) F. J. Ludwig and K. H. Adams, *ibid.*, **76**, 3853 (1954).

(21) K. B. Wiberg and R. J. Evans, *ibid.*, **80**, 3019 (1958).

(22) Unpublished results.

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Solutions of Metals in Amine Solvents. III. The Conductance of Dilute Solutions of Lithium in Methylamine at −78.3°[1]

BY DONALD S. BERNS,[2] E. CHARLES EVERS AND PAUL W. FRANK, JR.

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The conductance of lithium in methylamine at −78.3° has been measured over the concentration range from 0.22 N to 1.8×10^{-4} N. The data follow the conductance function proposed earlier[15] and provide further support for the model of metal–amine solutions proposed by Becker, Lindquist and Alder.[7]

Numerous theories have been proposed to account for the physical properties of solutions of metals in amine solvents.[3–10] Of those theories currently in favor, which pertain to dilute metal solutions, we prefer that proposed by Becker, Lindquist and Alder.[7] These authors suggest that "solvated electrons" interact with solvated metal ions to form ion-pairs or "monomers"; the latter then interact to form diamagnetic quadrupoles or "dimers"; the four species are in dynamic equilibrium. This model appears to account well for many of the physical properties of solutions of metals in ammonia, although precise data are lacking in most instances. Recent, direct support for the model may be found in nuclear magnetic resonance studies of McConnell and Holm[11] in conjunction with a theoretical interpretation of their results by Blumberg and Das.[12]

The most precise data relating to dilute solutions of metals are those due to Kraus[13] on the conductance of sodium in liquid ammonia at −34°. Recently Evers and Frank,[14] using the mass action concept of Becker, *et al.*,[7] have derived a conductance function which successfully reproduced the data of Kraus up to concentrations in the neighborhood of 0.04 N. Since precise data were not avail-

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(3) C. A. Kraus, *J. Franklin Inst.*, **212**, 537 (1931).

(4) S. Freed and N. Sugarman, *J. Chem. Phys.*, **11**, 354 (1943).

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(6) J. Kaplan and C. Kittle, *ibid.*, **21**, 1429 (1953).

(7) E. Becker, R. H. Lindquist and B. J. Alder, *ibid.*, **25**, 971 (1956).

(8) M. F. Deigen and Yu. A. Tsvirko, *Ukrain. Fiz. Zhur.*, **1**, 245 (1956).

(9) J. F. Dewald and G. Lepoutre, THIS JOURNAL, **76**, 3369 (1954).

(10) J. Jortner, *J. Chem. Phys.*, **30**, 839 (1959).

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