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INFLUENCE OF IONIC ASSOCIATION ON VISCOSITY OF ELECTROLYTE SOLUTIONS

I. A NEW APPROACH TO THE JONES-DOLE EQUATION

The extended forms of Jones-Dole equations have been proposed taking into account the occurence of ionic equilibria in electrolyte solutions of the type KA_2, K_2A and K_3A where K means cation and A anion respectively.

The viscosity measurements in electrolyte solutions are one of the methods which allowed us to the more comprehensive description of ion-ion and ion-dipoles of solvent interactions. This is one of the methods of study phenomen of ionic solvatation. Up till now several equations describing relationship between viscosity and concentration of electrolyte in solution have been suggested. One of mostly applied is the Jones-Dole equation [1]:

$$\eta/\eta_o = \eta_r = 1 + Ac^{1/2} + Bc \tag{1}$$

where:

η_r - is relative viscosity of solution,

η and η_o - the dynamic viscisities of solution and solvent respectively,

c - is molar concentration of electrolyte.

The coefficient A is connected with electrostatic ion-ion interactions and can be calculated from Falkenhagen equation [2].

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The excellent agreement of the empirical A coefficients and theoretical ones was confirmed in aqueous solutions. In organic and mixed solvent the agreement is poorer especially in the case where ionic association occurs [3]. The obtained empirically coefficient B is a measure of the ion-solvent interaction and is a sum of ionic contributions for cation and anion.

Interpretation of the values of B coefficient may be based on the different models [4-7]. Especially the values of $\partial B/\partial T$ coefficient afford valuable conclusion [8-12] with regard to the effect of the electrolyte on the the solvent structure.

The Jones-Dole in form (1) is obeyed in the limited concentration range of electrolyte e.g. in water to ca. 0.1 $\mathrm{mol \cdot dm^{-3}}$. In organic and mixed solvents the range of concentration should be determined experimentally for each electrolyte and occasionally terms involving higher powers of the molar concentration must be added and equation (1) can be written in the following form:

$$\eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \tag{2}$$

The majority of the literature data of viscosity for electrolyte solutions concern the 1-1 electrolytes and the influence of ionic association on viscosty is not usually taken into account. Ionic association causes that the concentration of ions is lower than the electrolyte one and B coefficient, being a measure of electrolyte solvent interaction, is not a simple sum of B_{K^+} and B_{A^-}.

Hence interaction undissociated part of electrolyte for example an ion pair with solvent should be also taken into consideration. Therefore if ionic association, connected with the process:

$$K^+ + A^- \xrightleftharpoons{Ka} KA$$

occurs equation (1) takes the following form:

$$\eta_r = 1 + A\sqrt{\alpha c} + B_1 \alpha c + B_0(1 - \alpha)c \tag{3}$$

where:

α - the degree of dissociation,

K_a - the association constant,

B_1 - B coefficient for ions: $B_1 = B_{K^+} + B_{A^-}$;
B_0 - B coefficient for undissociated form of electrolyte.

The degree of dissociation, can be obtained from association constant using the relations:

$$K_a = \frac{1-\alpha}{\alpha^2 c y_\pm^2} \qquad (3a)$$

$$\ln y_\pm = \frac{-A_{DH}\sqrt{\alpha c}}{1 + R B_{DH}\sqrt{\alpha c}} \qquad (3b)$$

where:

$y_\pm$ - mean molar activity coefficient;
A_{DH}, B_{DH} - coefficients of the Debye-Hückel equation;
R - distance parameter of ions.

Davies and Malpass [13] used equation (3) for description of viscisity in electrolyte solutions.

In the case of electrolytes KA_2 type two possible equilibria may be exist:

$$KA^+ + A^- \underset{K_{d1}}{\overset{K_{a1}}{\rightleftarrows}} KA_2 \qquad (4)$$

$$K^{+2} + A^- \underset{K_{d2}}{\overset{K_{a2}}{\rightleftarrows}} KA^+ \qquad (5)$$

where:

K_a - association constant,
K_d - dissociation constant.

For each of them i.e. (4) and (5), respectively, the association constants, K_a, may be written:

$$K_{a1} = \frac{c_{KA_2} y_{KA_2}}{c_{KA^+}\, c_{A^-}\, y_{KA^+}\, y_{A^-}} \qquad (6)$$

$$K_{a2} = \frac{c_{KA^+}\, y_{KA^+}}{c_{K^{+2}}\, c_{A^-}\, y_{K^{+2}}\, y_{A^-}} \tag{7}$$

Taking $y_{A^-} = y_{KA^+} = y^{\pm}$ and $y_{KA_2} = 1$ and also describing concentrations in following way:

$$c_{KA_2} = c(1 - \alpha_1)$$

$$c_{KA^+} = c\alpha_1(1 - \alpha_2)$$

$$c_{A^-} = c\alpha_1(1 + \alpha_2)$$

$$c_{K^{+2}} = c\,\alpha_1\alpha_2 \tag{8}$$

equation (6) and (7) can be written in forms:

$$K_{a1} = \frac{1 - \alpha_1}{c\alpha_1^2(1 - \alpha_2^2)y_{\pm}^2} \tag{9}$$

$$K_{a2} = \frac{1 - \alpha_2}{c\alpha_1\alpha_2(1 + \alpha_2)\, y_{K^{+2}}} \tag{10}$$

Very frequently the equilibria (4) and (5) satisfy the condition

$$0 \simeq K_{a1} \ll K_{a2} \tag{11}$$

which means, that in the solution undissociated form, KA_2, does not practically exist, that is $\alpha_1 = 1$. Thus only the equilibrium (5) describes electrolyte solution and the association constant, K_{a2}, may be written in forms:

$$K_{a2} = \frac{1 - \alpha_2}{c\alpha_2(1 + \alpha_2)y_{K^{+2}}} \tag{12}$$

In this special case the Jones-Dole equation should be written in form [14]:

$$\eta_r = 1 + A\sqrt{c\alpha_2} + B_{K^{+2}} c_{K^{+2}} + B_{KA^+} c_{KA^+} + B_{A^-} c_{A^-}$$

or

$$\eta_r = 1 + A\sqrt{c\alpha_2} + B_{K^{+2}} c\alpha_2 + B_{KA^+} c(1 - \alpha_2) + B_{A^-} c(1 + \alpha_2)$$

which may be transform into form:

$$\eta_r = 1 + A\sqrt{c\alpha_2} + (B_{K^{+2}} + 2B_{A^-}) c\alpha_2 + (B_{KA^+} + B_{A^-}) c(1 - \alpha_2) \quad (13)$$

Denoting: $B_{K^{+2}} + 2B_{A^-} = B_2$, $B_{KA^+} + B_{A^-} = B_1$, $\alpha = \alpha_2$ the following relationship is obtained:

$$\eta_r = 1 + A\sqrt{c\alpha} + B_2 c\alpha + B_1 c(1 - \alpha) \quad (14)$$

Such form of Jones-Dole equation was used by Quintana et al. [14] in order to obtain the B_1 and B_2 coefficient for Na_2SO_4 in water-etanol mixtures. They used the salt of K_2A type and in that case: $B_2 = B_{A^{-2}} + 2B_{K^+}$ and $B_1 = B_{KA^-} + B_{K^+}$ where: $K^+ = Na^+$ and $A^{-2} = SO_4^{-2}$.

Assuming $\alpha_1 = 1$ the whole concentration of electrolyte can be divide formally into two parts which dissociate according to equations:

$$\text{part 1} \quad KA_2^{(1)} \longrightarrow KA^+ + A^- \quad \text{as symmetrical electrolyte}$$

$$\text{part 2} \quad KA_2^{(2)} \longrightarrow K^{+2} + 2A^- \quad \text{as asymmetrical electrolyte} \quad (15)$$

The concentration $c(1 - \alpha_2)$ corresponds the part 1 and $c\alpha_2$ the part 2 respectively. Proportion between both contributions dependent on concentration of electrolyte i.e. at the lower concentration the quantitative contribution of the part 2 increases. At $c = 0$ this contribution becomes total i.e. electrolyte is completely dissociated according to the scheme:

$$KA_2 \rightarrow K^{+2} + 2A^- \quad \text{and} \quad c_{K^{+2}} = c, \; c_{A^-} = 2c$$

The coefficient A of Jones-Dole equation is connected with long-range interionic interactions and can be calculated from the Falkenhagen equation [2]:

$$A = \frac{1.461}{\eta_0(\varepsilon_0 T)^{1/2}}\left[\frac{\nu_1|Z_1|}{|Z_1| + |Z_2|}\right]^{1/2} \frac{1}{\lambda_1^0\ \lambda_2^0}\ \psi \qquad (16)$$

where ν_1 is the number of types of the ions formed from molecule and

$$\psi = \frac{\lambda_1^0 Z_2^2 + \lambda_2^0 Z_1^2}{4} - \frac{(|Z_2|\ \lambda_1^0 - |Z_1|\ \lambda_2^0)^2}{\left[\sqrt{\lambda_1^0 + \lambda_2^0} + \sqrt{|Z_2|\ \lambda_1^0 + |Z_1|\ \lambda_2^0}\left[\frac{|Z_1| + |Z_2|}{|Z_1 Z_2|}\right]^{1/2}\right]^2}$$

The other symbols have their usual meaning.

As it seen the value of A depend on the type of electrolyte and the limmiting ionic mobility.

In the case if all equilibria described equations (4) and (5) take place $\alpha_1 < 1$ then in solution all chemical forms exist and their concentrations are described equations (8).

Hence electrolyte may be treated as the composed of three forms:

$KA_2^{(0)}$ - undissociated one,

$KA_2^{(1)}$ - dissociated one according to the scheme $KA_2 \rightarrow KA^+ + A^-$,

$KA_2^{(2)}$ - dissociated one according to the scheme $KA_2 \rightarrow K^{+2} + 2A^-$.

The concentrations: $c(1 - \alpha_1)$, $c\alpha_1(1 - \alpha_2)$ and $c\alpha_1\alpha_2$ correspond these forms $KA_2^{(0)}$, $KA_2^{(1)}$ and $KA_2^{(2)}$, respectively.

In this most general case the Jones-Dole equation for electrolyte of KA_2 type may be taken on form equation (17)

$$\eta_r = 1 + A\sqrt{c\alpha_1\alpha_2} + \alpha_1[B_1 c(1 - \alpha_2) + B_2 c\alpha_2] + c(1 - \alpha_1)B_0 \qquad (17)$$

where:

$$B_0 = B_{KA_2},\ B_1 = B_{KA^+} + B_{A^-},\ B_2 = B_{K^{+2}} + 2B_{A^-}$$

In the case of electrolyte of K_2A type it will be:

$B_0 = B_{KA_2}$, $B_1 = B_{KA^-} + B_{K^+}$, $B_2 = B_{A^{-2}} + 2B_{K^+}$ respectively.

Assuming $K_{a1} \ll K_{a2}$ and $\alpha_1 = 1$ the form KA_2 is practically absent in the solution equation (17) takes on form (18) identical with equation (14)

$$\eta_r = 1 + A\sqrt{c\alpha_2} + B_1 c(1 - \alpha_2) + B_2 c\alpha_2 \qquad (18)$$

As besides K_{a2} has inconsiderable value i.e. $\alpha_2 \approx 1$ then equation (18) can be written in form:

$$\eta_r = 1 + A_2\sqrt{c} + Bc$$

identical with one for completely dissociated electrolytes of KA_2 type.

For unsymetrical electrolytes of KA_3 or K_3A type the following possible equilibria should be taken into account:

For unsymmetrical electrolytes of KA_3 or K_3A type the following

$$KA_2^+ + A^- \underset{K_{d1}}{\overset{K_{a1}}{\rightleftarrows}} KA_3 \qquad (19a)$$

$$KA^{+2} + A^- \underset{K_{d2}}{\overset{K_{a2}}{\rightleftarrows}} KA_2^+ \qquad (19b)$$

$$K^{+3} + A^- \underset{K_{d3}}{\overset{K_{a3}}{\rightleftarrows}} KA^{+2} \qquad (19c)$$

and the association constants can be written for then, respectively:

$$K_{a1} = \frac{c_{KA_3}\, y_{KA_3}}{c_{KA_2^+}\, c_{A^-}\, y_{KA_2^+}\, y_{A^-}} \qquad (20a)$$

$$K_{a2} = \frac{c_{KA_2^+}\, y_{KA_2^+}}{c_{KA^{+2}}\, c_{A^-}\, y_{KA^+}{}^{2} y_{A^-}} \qquad (20b)$$

$$K_{a3} = \frac{c_{KA^+}\, y_{KA^+}}{c_{K^{+3}}\, c_{A^-}\, y_{K^{+3}}\, y_{A^-}} \qquad (20c)$$

If α_1, α_2 and α_3 denote the degree of dissociation corresponding to equilibria (19a), (19b) and (19c), respectively, the concentration of all possible form of ions and undissociated electrolyte can be obtained from equations (21)

$$c_{KA_3} = (1 - \alpha_1)c \qquad (21a)$$

$$c_{KA_3} = \alpha_1(1 - \alpha_2)c \qquad (21b)$$

$$c_{KA^{+2}} = \alpha_1\alpha_2(1 - \alpha_3)c \qquad (21c)$$

$$c_{K^{+3}} = \alpha_1 c + \alpha_1\alpha_2 c + \alpha_1\alpha_2\alpha_3 c \qquad (21d)$$

$$c_{K^{+3}} = \alpha_1\alpha_2\alpha_3 c \qquad (21e)$$

When the determined as above concentrations are substituted into equations (20a), (20b), (20c) then for

$$y_{KA_3} = 1 \text{ and } y_{KA_2^+} = y_{A^-}$$

equations (20) take forms:

$$K_{a1} = \frac{1 - \alpha_1}{\alpha_1^2(1 - \alpha_2)(1 + \alpha_2 + \alpha_2\alpha_3)c y_\pm^2} \qquad (22a)$$

$$K_{a2} = \frac{\alpha_1(1 - \alpha_2)}{\alpha_1^2\alpha_2(1 - \alpha_3)(1 + \alpha_2 + \alpha_2\alpha_3)c y_{KA^{+2}}} \qquad (22b)$$

$$K_{a3} = \frac{\alpha_1\alpha_2(1 - \alpha_3)y_{KA^{+2}}}{\alpha_1^2\alpha_2\alpha_3(1 + \alpha_2 + \alpha_2\alpha_3)c y_\pm\, y_{K^{+3}}} \qquad (22c)$$

If all equilibria (19) occur and all possible chemical forms of electrolyte exist their concentrations are expressed by equation (21), electrolyte may be considered as composed of four parts

$KA_3^{(0)}$ - undisociated one,

$KA_3^{(1)}$ - dissociated one according to the scheme: $KA_3 \rightarrow KA_2^+ + A^-$,

$KA_3^{(2)}$ - dissociated one according to the scheme: $KA_3 \rightarrow KA^{+2} + 2A^-$,

$KA_3^{(3)}$ - dissociated one according to the scheme: $KA_3 \rightarrow K^{+3} + 3A^-$.

The concentrations $c(1 - \alpha_1)$, $c\alpha_1(1 - \alpha_2)$, $c\alpha_1\alpha_2(1 - \alpha_3)$ and $c\alpha_1\alpha_2\alpha_3$ correspond the forms $KA_3^{(0)}$, $KA_3^{(1)}$, $KA_3^{(2)}$ and $KA_3^{(3)}$, respectively.

In the above case for electrolyte of KA_3 type the Jones-Dole equation should be presented in form (23a)

$$\eta_r = 1 + A\sqrt{c\alpha_1\alpha_2\alpha_3} + \alpha_1[B_1(1 - \alpha_2)c + B_2\alpha_2(1 - \alpha_3)c + B_3\alpha_2\alpha_3 c] + + (1 - \alpha_1)cB_0 \qquad (23a)$$

where:

$B_0 = B_{KA_3}$,

$B_1 = B_{KA_2^+} + B_{A^-}$,

$B_2 = B_{KA^{+2}} + 2B_{A^-}$,

$B_3 = B_{K^{+3}} + 3B_{A^-}$.

In the case of electrolyte K_3A type it will be:

$$B_0 = B_{K_3A},\ B_1 = B_{K^+} + B_{K_2A^-},\ B_2 = 2B_{K^+} + B_{KA^{-2}},\ B_3 = 3B_{K^+} + B_{A^{-3}}$$

respectively.

The Jones-Dole equation for KA_3 electrolyte shown in form (23a) is mostly general equation taking into consideration the possibility of occurance of electrolyte in different chemical forms, which concentration depend on the values of association constants K_{a1}, K_{a2}, K_{a3} and the molar concentration of electrolyte.

Usually the equilibrium constants obey the inequality $K_{a1} < K_{a2} < K_{a3}$. Then $\alpha_1 = 1$ and equation (23a) should be modified ($K_{a1} \cong 0$):

$$\eta_r = 1 + A\sqrt{c\alpha_2\alpha_3} + B_1(1 - \alpha_2)c + B_2\alpha_2(1 - \alpha_3) + B_3\alpha_2\alpha_3 c \qquad (23b)$$

When moreover $K_{a2} < K_{a3}$ and $\alpha_2 \cong 1$ equation (23b) is given by

$$\eta_r = 1 + A\sqrt{c\alpha_3} + B_2c(1 - \alpha_3) + B_3c\alpha_3 \qquad (23c)$$

If also K_{a3} reaches not large values and $\alpha_3 \cong 1$ then equation (23a) can be written in a form:

$$\eta_r = 1 + A\sqrt{c} + B_3c \qquad (23d)$$

which is characteristic for completely dissociated electrolytes of KA_3 or K_3A type.

Summarizing the suggested approaches to the Jones-Dole equation include influence of ion-ion and ion-dipole of solvent interaction for all ions and ion pairs existing in solution. The complete forms of these equations for electrolyte of KA_2 type i.e. equation (17) and especially for KA_3 one equation (23a) are evidently complicated. However the limiting equivalent conductivities of ions and the association constants, determined from the conductivity measurements, enable to calculate the values of A coefficients from the Falkenhagen equation and the degrees of dissociation of electrolyte in an iterative procedure. The values of B coefficients corresponding to specified ions and ion pairs can be obtained from series of η_r and c data by use of suitable methods.

The review of the proper methods to enable to solution suggested abo forms of the Jones-Dole equation was made in paper [15].

REFERENCES

[1] G. Jones, M. Dole, J. Amer. Chem. Soc., 51, 2950 (1929).

[2] T. Erdey-Gruz, Transport Phenomena in Aqueous Solutions, Budapest 1974, p.128.

[3] J. Crudden, G. M. Delaney, D. Feakins, P. J. O'Reilly, W. E. Waghorne, K. G. Lawrence, J. Chem. Soc. Faraday Trans. I, 82, 2195, 2207 (1985).

[4] W. M. Cox, J. H. Wolfenden, Proc. Roy. Soc., A 145, 475 (1934).

[5] R. S. Stokes, R. Mills, Viscosity of Electrolytes and Related Properties. Pergamon Press Inc., New York 1961.

[6] B. S. Krumgaltz, J. Phys. Chem., 83, 763 (1979).

[7] D. Feakins, D. J. Freemantle, G. K. Lawrence, J. Chem. Soc. Faraday Trans. I, 70, 795 (1974).

[8] M. Kaminsky, Disc. Faraday Soc., 24, 171 (1951).

[9] D. J. P. Out, J. M. Los, J. Solution Chem., 9, 1 (1980).

[10] M. Kaminsky, Z. Naturf., 12a, 424 (1957).

[11] E. R. Nigtingale, J. Phys. Chem., 63, 138, 742 (1959).

[12] I. M. Tsangaris, M. R. Bruce, Arch. Biochem. and Biophys., 112, 269 (1965).

[13] C. W. Davies, V. E. Malpass, Trans. Faraday Soc., 72, 2075 (1964).

[14] C. Quintana, M. L. Llorente, M. Sanches, A. Vivo, J. Chem. Soc. Faraday Trans. I, 82, 3307 (1986).

[15] A. Bald, Acta Univ. Lodz., Folia Chim., 9, 45 (1991).

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WPŁYW ASOCJACJI JONOWEJ NA LEPKOŚĆ ROZTWORÓW ELEKTROLITÓW
I. NOWE POSTACIE RÓWNANIA JONESA-DOLE'A

Zaproponowano rozszerzone wersje równania Jonesa-Dole'a, które uwzględniają równowagi jonowe występujące w roztworach elektrolitów niecałkowicie zdysocjowanych typu KA_2, K_2A, KA_3 i K_3A, gdzie: K - kation, A - anion. Współczynniki A i B proponowanych równań związane z oddziaływaniami typu jon-jon i jon-rozpuszczalnik przypisano ściśle określonym jonom i parom jonowym.