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INFLUENCE OF IONIC ASSOCIATION ON VISCOSITY
OF ELECTROLYTE SOLUTIONS

II. METHODS OF DETERMINATION OF THE JONES-DOLE EQUATION

Several methods of solving the forms of the Jones-Dole equatation presented earlier [1] have been suggested for incompletely dissociated electrolytes of KA, KA_2, K_2A, KA_3 and K_3A types where K and A are cation and anion, respectively. The different variants taking into account the values of ionic equilibrium constant have been considered. The aim of sugested methods is the correct determination of B coefficients of the Jones-Dole equation.

ELECTROLYTES OF KA TYPE

In the case of 1-1 electrolytes which are comletely dissociated the Jones-Dole equation is given in the form:

$$\eta_r = 1 + A\sqrt{c} + Bc \qquad (1)$$

or at higher concentrations of electrolyte

$$\eta_r = 1 + A\sqrt{c} + Bc + Dc^2 \qquad (2)$$

The A and B coefficients can be determined if the above equations are rearranged to the forms:

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$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} \tag{1a}$$

and

$$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c} + Dc^{3/2} \tag{2a}$$

Reationship (1a) is polynominal of first order in relation to $\sqrt{c}$. Using the least squares method the A and B coefficient can be calculated. Relation (2a) is polynominal of third order in relation to $\sqrt{c}$ and the least squares method lets us to determine the all A, B and D coefficients. They can be also calculated by use other methods proposed by M a r t i n u s et al. [2]. In my opinion the more certain way of the determination the all parameters of equations (1) and (2) is based on using in the calculations the theoretical A coefficients. That is because for other solutions than in water the agreement of the values of theoretical and empirical A coefficients is not really sufficient [3]. Hence A should be obtain from the F a l k e n h a g e n equation [4].

$$A = \frac{1.461}{\eta_0 (\varepsilon_0 T)^{1/2}} \left[\frac{\nu_1 |z_1|}{|z_1| + |z_2|} \right]^{1/2} \frac{1}{\lambda_1^0 \lambda_2^0} \psi \tag{3}$$

$$\psi = \frac{\lambda_1^0 z_2^2 + \lambda_2^0 z_1^2}{4} - \frac{(|z_2|\lambda_1^0 - |z_1|\lambda_2^0)^2}{\left[\sqrt{\lambda_1^0 + \lambda_2^0} + \sqrt{|z_2|\lambda_1^0 + |z_1|\lambda_2^0} \left[\frac{|z_1| + |z_2|}{|z_1 z_2|} \right]^{1/2} \right]^2}$$

The symbols in equation (3) have their usual meaning. Therefore, the limiting ionic ionic conductivities are required which may be determined from conductivity measurements in electrolyte solutions. If the A coefficient are known, equations (1) and (2) can be rearranged in the following way

$$\frac{\eta_r - 1 - A\sqrt{c}}{c} = B \tag{1b}$$

and

$$\frac{\eta_r - 1 - A\sqrt{c}}{c} = B + Dc \tag{2b}$$

Equation (1b) and (2b) can be treated as polyniminal of zero and first order against of molar concentration, c, respectively. The solution of equation (1b) reduces then to calculation of the arithmetic mean and equation (2b) can be solved the least squares method. The above ways of calculation coefficients give really the better results because of the lower number of calculated parameters. Solving equation (1b) and (2b) the indispensability of taking into account the D coefficient can be also estimate. When electrolyte is not quite dissociated the equilibrium of the process: $K^+ + A^-$ $\xrightleftharpoons{Ka}$ KA can be described the association constant:

$$K_a = \frac{1 - \alpha}{c\alpha^2 y_\pm^2}$$

where α is the degree of dissociation and $y_\pm$ the mean activity coefficient. The Jones-Dole equation for this case, accordingly with D a v i e s and M a l p a s s [5], is given by:

$$\eta_r = 1 + A\sqrt{c} + B_i c\alpha + B_p c(1 - \alpha) \tag{4a}$$

where $B_i = B_{K^+} + B_{A^-}$, and B_p is coefficient of ion pair.

Equation (4a) may be rearranged to the form:

$$\frac{\eta_r - 1A\sqrt{c}}{c\alpha} = B_i + B_p \frac{1 - \alpha}{\alpha} \tag{4b}$$

and hence the B_i and B_p coefficients can be obtained by the least squares method. The values of A coefficients can be obtained in two ways. The first one [6] is based on the extrapolation $\eta_r - 1/\sqrt{c}$ vs. $\sqrt{c}$, taking the intercepts at $\sqrt{c} = 0$ as the required A values and assumption that the obtained A values are correct. The second one [3] is based on the calculation the A values from equation (3) taking the obtained previously values of ionic conductivities.

The last - mentioned one is more sensible in my opinion.

The values of the degree of dissociation at each concentration used can be iteratively calculated from the following equations:

$$K_a = \frac{1 - \alpha}{c\alpha^2 y_\pm^2} \tag{5a}$$

$$\ln y_\pm = \frac{-A_{DH}\sqrt{I}}{1 + RB_{DH}\sqrt{I}} \tag{5b}$$

where:

R - is the distance of closest approach of ions,

I - the ionic force of electrolyte $\sqrt{I} = c\alpha$.

The mentioned above both methods methods of solution of equation (4a) are based on indipendent determination of the A coefficients and linearisation of equation (4a) to the easily solvable form (4b). In my opinion equation (4a) can be solved using the nonlinear least squares methods with simultaneous determination of all its parameters i.e. A, B_i and B_p.

From equation (4a) and definition of the total differential it follows that:

$$\Delta\eta_r = \frac{\partial\eta_r}{\partial A} \Delta A + \frac{\partial\eta_r}{\partial B_i} \Delta B_i + \frac{\partial\eta_r}{\partial B_p} \Delta B_p \tag{6}$$

where:

$$\frac{\partial\eta_r}{\partial A} = \sqrt{c\alpha},$$

$$\frac{\partial\eta_r}{\partial B_i} = c\alpha,$$

$$\frac{\partial\eta_r}{\partial B_p} = c(1 - \alpha),$$

$$\Delta\eta_r = \eta_{r,exp.} - \eta_{r,calc.}$$

Applying the least squares method to the equation (6) the system of equation (7) is obtained:

$$\Delta A \sum \left[\frac{\partial \eta_r}{\partial A}\right]_i \left[\frac{\partial \eta_r}{\partial A}\right]_i + \Delta B_i \sum \left[\frac{\partial \eta_r}{\partial B_i}\right]_i \left[\frac{\partial \eta_r}{\partial A}\right]_i + \Delta B_p \sum \left[\frac{\partial \eta_r}{\partial B_p}\right]_i \left[\frac{\partial \eta_r}{\partial A}\right]_i =$$

$$= \sum \Delta \eta_r {}_i \left[\frac{\partial \eta_r}{\partial A}\right]_i$$

$$\Delta A \sum \left[\frac{\partial \eta_r}{\partial A}\right]_i \left[\frac{\partial \eta_r}{\partial B_i}\right]_i + \Delta B_i \sum \left[\frac{\partial \eta_r}{\partial B_i}\right]_i \left[\frac{\partial \eta_r}{\partial B_i}\right]_i + \Delta B_p \sum \left[\frac{\partial \eta_r}{\partial B_p}\right]_i \left[\frac{\partial \eta_r}{\partial B_i}\right]_i =$$

$$= \sum \Delta \eta_r {}_i \left[\frac{\partial \eta_r}{\partial B_i}\right]_i$$

$$\Delta A \sum \left[\frac{\partial \eta_r}{\partial A}\right]_i \left[\frac{\partial \eta_r}{\partial B_p}\right]_i + \Delta B_i \sum \left[\frac{\partial \eta_r}{\partial B_i}\right]_i \left[\frac{\partial \eta_r}{\partial B_p}\right]_i + \Delta B_p \sum \left[\frac{\partial \eta_r}{\partial B_p}\right]_i \left[\frac{\partial \eta_r}{\partial B_p}\right]_i =$$

$$= \sum \Delta \eta_r {}_i \left[\frac{\partial \eta_r}{\partial B_p}\right]_i \tag{7}$$

where the unknown quantity are increments of ΔA, ΔB_i and ΔB_p.

The first step in calculation must be an evaluation of the initial values of $A^{(0)}$, $B_i^{(0)}$ and $B_p^{(0)}$. Then the k_a values are used to calculate the degree of dissociation, α, from equations (5) and the $\Delta \eta_r$, $\partial \eta_r / \partial A$, $\partial \eta_r / \partial B_i$, and $\partial \eta_r / \partial B_p$ values for all experimental points. The next suitable sums, occuring in equation system (7), are calculated and $A^{(1)}$, $B_i^{(1)}$ and $B_p^{(1)}$ are obtained solving it. As a result it allows us to evaluate more precisely the values of: $A^{(1)} = A^{(0)} + \Delta A^{(1)}$, $B_i^{(1)} = B_i^{(0)} + \Delta B_i^{(1)}$ and $B_p^{(1)} = B_i^{(0)} + \Delta B_p^{(1)}$. Then the all calculation procedure is repeated taking into account as the initial values $A^{(1)}$, $B_i^{(1)}$ and $B_p^{(1)}$ getting in the second cycle of calculation the next correct values of searched coefficients.

The calculations are finished if:

$$\sigma \eta_r^{(k)} - \sigma \eta_r^{(k+1)} < \sigma \tag{8}$$

where:

σ - the experimental error of η_r,

$$\sigma \eta_r = \sqrt{\frac{\Sigma(\eta_{r,exp.} - \eta_{r,calc.})^2}{n-3}}$$

k - number of calculation cycle,

n - number of measurement.

It should point out that taking into consideration the number of parallel searching parameters the above-method can be used only for data of high precision.

ELECTROLYTES OF KA_2 AND K_2A TYPES

I was reported earlier [1] that in electrolyte solution of KA_2 type the following equilibria can be expectet:

$$KA^+ + A^- \xrightleftharpoons{K_{a1}} KA_2 \quad \text{and} \quad K^{+2} + A^- \xrightleftharpoons{K_{a2}} KA^+$$
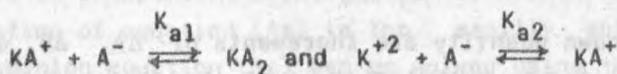
for which the equilibrium constants are expressed:

$$K_{a1} = \frac{1 - \alpha_1}{c\alpha_1^2(1 - \alpha_2^2)y_{\pm}^2} \tag{10}$$

$$K_{a2} = \frac{1 - \alpha_2}{c\alpha_1\alpha_2(1 + \alpha_2)y_K^{+2}} \tag{11}$$

where

$$\ln y_{\pm} = -\frac{A_{DH}\sqrt{I}}{1 + RB_{DH}\sqrt{I}} \tag{12}$$

$$\ln y_{K^{+2}} = -\frac{4A_{DH}\sqrt{I}}{1 + RB_{DH}\sqrt{I}} \tag{13}$$

$$I = c\alpha_1(1 + 2\alpha_2)$$

In equation (12) and (13) the A_{DH} and B_{DH} coefficients are the Debye-Hückel ones. The parameter of the closest approach of ions, R, according to Justice's suggestion, can be assumed to the Bjerrum's distance $q = |z_1 z_2| e^2 / 2kT$ [7, 8].

The J o n e s-D o l e equation takes the general form [1]

$$\eta_r = 1 + A\sqrt{c\alpha_1\alpha_2} + \alpha_1[B_1 c(1 - \alpha_2) + B_2 c\alpha_2] + c(1 - \alpha_1)B_0 \quad (14)$$

where α_1 and α_2 are the degrees of dissociations related to the K_{a1} and K_{a2} equilibrium constants, respectively. The K_{a1} and K_{a2} values may be found from conductivity measurement of electrolyte solutions.

The degrees of dissociation α_1 and α_2 for each electrolyte concentration used are calculated from K_{a1} and K_{a2} solving the equation system (10)-(13) using the iterative method of succesive approximations. In this aim subroutine called ALFA 12 can be used.

Equation (14) contains as many as 4 unknown parameters. The simultaneously calculation of them would be, in my opinion, theoretically possible using the nonlinear least squares method if the whole procedure was converged. The obtained results would be burden with significant errors. It is more reasonably to determine the limiting ionic conductivities from conductivity measurements in electrolyte solutions and using them to calculate the A coefficient from equation (3).

The other parameters B_1, B_2 and B_0 can be calculated in two ways:

1^0 Using equation (14) in the form of total differential

$$\Delta\eta_r = \frac{\partial\eta_r}{\partial B_1} \cdot \Delta B_1 + \frac{\partial\eta_r}{\partial B_2} \Delta B_2 + \frac{\partial\eta_r}{\partial B_0} \Delta B_0 \quad (15)$$

where $\partial\eta_r/\partial B_0 = c(1 - \alpha_1)$, $\partial\eta_r/\partial B_1 = c\alpha_1(1 - \alpha_2)$, $\partial\eta_r/\partial B_2 = c\alpha_1\alpha_2$ and from the application of the least squares method the following equation system can be written:

$$\Delta B_0 \sum \left[\frac{\partial \eta_r}{\partial B_0}\right]_i \left[\frac{\partial \eta_r}{\partial B_0}\right]_i + \Delta B_1 \sum \left[\frac{\partial \eta_r}{\partial B_1}\right]_i \left[\frac{\partial \eta_r}{\partial B_0}\right]_i + \Delta B_2 \sum \left[\frac{\partial \eta_r}{\partial B_2}\right]_i \left[\frac{\partial \eta_r}{\partial B_0}\right]_i =$$

$$= \sum \Delta \eta_{r,i} \left[\frac{\partial \eta_r}{\partial B_0}\right]_i$$

$$\Delta B_0 \sum \left[\frac{\partial \eta_r}{\partial B_0}\right]_i \left[\frac{\partial \eta_r}{\partial B_1}\right]_i + \Delta B_1 \sum \left[\frac{\partial \eta_r}{\partial B_1}\right]_i \left[\frac{\partial \eta_r}{\partial B_1}\right]_i + \Delta B_2 \sum \left[\frac{\partial \eta_r}{\partial B_2}\right]_i \left[\frac{\partial \eta_r}{\partial B_1}\right]_i =$$

$$= \sum \Delta \eta_{r,i} \left[\frac{\partial \eta_r}{\partial B_1}\right]_i$$

$$\Delta B_0 \sum \left[\frac{\partial \eta_r}{\partial B_0}\right]_i \left[\frac{\partial \eta_r}{\partial B_2}\right]_i + \Delta B_1 \sum \left[\frac{\partial \eta_r}{\partial B_1}\right]_i \left[\frac{\partial \eta_r}{\partial B_2}\right]_i + \Delta B \sum \left[\frac{\partial \eta_r}{\partial B_2}\right]_i \left[\frac{\partial \eta_r}{\partial B_2}\right]_i =$$

$$= \sum \Delta \eta_{r,i} \left[\frac{\partial \eta_r}{\partial B_2}\right]_i \tag{16}$$

Finding increments of ΔB_0, ΔB_1 and ΔB_2 the more precisely values of the B coefficients can be calculated and the whole procedure is repeated as mentioned above analogous method for incompletely dissociated 1-1 electrolytes.

2^0 Equation (14) may be linearized to the form:

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

The left hand - side of equation (17) can be calculated assuming the value of B_0 coefficient. Then B_1 and B_2 coefficients can be obtained from the least squares method. The calculation must be repeated for the B_0 values changing with the definite step till to find the minimum of the standard deviation of the function

$$\sigma_y = \sqrt{(y_{i,exp.} - y_{i,calc.})^2 / (n-3)}$$

establishing in this way the optimal values of the B_0, B_1 and B_2 coefficients.

It may be noticed that in both methods the experimental data of high precision should be used. Luckily, as a rule, $K_{a1} \ll K_{a2}$ and additionally $K_{a1} \approx 0$. In this case $\alpha_1 = 1$ and equation (14) has a form:

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

This equation can be solved with help of the both earlier proposed methods and only two parameters, B_1 and B_2, to be determined. Both the methods will be significanty simplified from the following reasons:

1^0 The determination of the α_2 value reduces to the iterative solution of the system

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

and

$$\ln y_{K^+2} = -\frac{4A_{DH}\sqrt{I}}{1 + RB_{DH}\sqrt{I}}$$

where $I = c(1 + 2\alpha_2)$.

2^0 In first method, above earlier, only the system of equations remains for solution:

$$\Delta B_1 \sum \left[\frac{\partial \eta_r}{\partial B_1}\right]_i \left[\frac{\partial \eta_r}{\partial B_1}\right]_i + \Delta B_2 \sum \left[\frac{\partial \eta_r}{\partial B_2}\right]_i \left[\frac{\partial \eta_r}{\partial B_1}\right]_i = \sum \left[\frac{\partial \eta_r}{\partial B_1}\right]_i \Delta \eta_{r,i}$$

$$\Delta B_1 \sum \left[\frac{\partial \eta_r}{\partial B_1}\right]_i \left[\frac{\partial \eta_r}{\partial B_2}\right]_i + \Delta B_2 \sum \left[\frac{\partial \eta_r}{\partial B_2}\right]_i \left[\frac{\partial \eta_r}{\partial B_2}\right]_i = \sum \left[\frac{\partial \eta_r}{\partial B_2}\right]_i \Delta \eta_{r,1}$$

3^0 In the second method, equation (18) can be rearranged to the form:

$$\frac{\eta_r - 1 - A\sqrt{c\alpha_2}}{c\alpha_2} = B_2 + B_1 \frac{1 - \alpha_2}{\alpha_2}$$

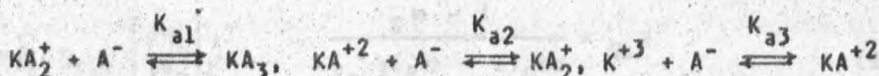where B_1 and B_2 coefficients are determined by the least suares method.

If also the K_{a2} value is very small then $\alpha_2 \approx 1$ and equation (18) changes its form to:

$$\eta_r = 1 + A\sqrt{c} + B_2 c \qquad (19)$$

characteristic for completly dissociated electrolyte and which can be solved by one from the earlier described methods.

ELECTROLYTE OF KA_3 AND K_3A TYPES

As it was reported earlier [1] in solution of electrolyte of KA_3 type the following equilibria can be expected:

$$KA_2^+ + A^- \overset{K_{a1}}{\rightleftharpoons} KA_3, \quad KA^{+2} + A^- \overset{K_{a2}}{\rightleftharpoons} KA_2^+, \quad K^{+3} + A^- \overset{K_{a3}}{\rightleftharpoons} KA^{+2}$$

characterized by the constants:

$$K_{a1} = \frac{1 - \alpha_1}{\alpha_1^2(1 - \alpha_2)(1 + \alpha_2 + \alpha_2\alpha_3)cy_\pm^2} \qquad (20)$$

$$K_{a2} = \frac{\alpha_1(1 - \alpha_2)}{\alpha_1^2\alpha_2(1 - \alpha_3)(1 + \alpha_2 + \alpha_2\alpha_3)cy_{KA^{+2}}} \qquad (21)$$

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

where:

$$\ln y_\pm = -\frac{A_{DH}\sqrt{I}}{1 + RB_{DH}\sqrt{I}} \qquad (23)$$

$$\ln y_{KA^{+2}} = -\frac{4A_{DH}\sqrt{I}}{1 + RB_{DH}\sqrt{I}} \qquad (24)$$

$$\ln y_{K^{+3}} = - \frac{9A_{DH} \sqrt{I}}{1 + RB_{DH} \sqrt{I}} \qquad (25)$$

and $I = 2\alpha_1\alpha_2(1 + 3\alpha_3)c$.

In the case of solution of electrolyte of KA_3 type the Jones--Dole equation has the form [1]:

$$\eta_r = 1 + A\sqrt{c\alpha_1\alpha_2\alpha_3} + \alpha_1[B_1(1 - \alpha_2)c + B_2\alpha_2(1 - \alpha_3)c + B_3\alpha_2\alpha_3c] +$$

$$+ (1 - \alpha_1)cB_0 \qquad (26)$$

If the values of K_{a1}, K_{a2} and K_{a3} are known, the dissociation degrees α_1, α_2 and α_3 for each concentration, c, can be itera- tively estimated. The subroutine ALFA 123, with considerably more advanced algorithm than mentioned above subroutine ALFA 12, may be applied for it.

With the aim of reducing the number of parameters (five) the values of ionic conductivities should be indipendently obtained (i.e. by measurement of electrical conductivity of electrolyte so- lutions) and the A coefficients calculated from equation (3).

Similary as in the case of electrolyte of KA_2 type the two methods of determination of the B_0, B_1, B_2 and B_3 coefficients can be used.

1^0 From the ralationship:

$$\eta_r = \frac{\partial \eta_r}{\partial B_0} \Delta B_0 + \frac{\partial \eta_r}{\partial B_1} \Delta B_1 + \frac{\partial \eta_r}{\partial B_2} \Delta B_2 + \frac{\partial \eta_r}{\partial B_3} \Delta B_3$$

and by applying the nonlinear least squares method the equation system is constructed, from which succesively decreasing increments of ΔB_0, ΔB_1, ΔB_2 and ΔB_3 values are determined and finally the proper values of the B coefficients are obtained.

2^0 Linearizing equation (26) we have:

$$y = \frac{\eta_r - 1 - A\sqrt{c\alpha_1\alpha_2\alpha_3} - B_0c(1 - \alpha_1) - B_1c\alpha_1(1 - \alpha_2)}{c\alpha_1\alpha_2\alpha_3}$$

$$= B_3 + B_2 \frac{1 - \alpha_3}{\alpha_3} \qquad (27)$$

The left - hand side of the above equation is calculated assuming the B_0 and B_1 coefficients. The B_2 and J_3 values are determined by the least squares method. The calculation must be repeated for B_0 and B_1 changed with fixed step down to the minimum of the standard deviation, σ_y. This procedure optimizes the values of B_0, B_1, B_2 and B_3 coefficients. In my opinion the first method is in this case much more effective for solving equation (26). Accuracy of the experimental must be extremely high and the number of data relatively large.

Generally, the equilibrium constants fulfilled the inequality $K_{a3} > K_{a2} > K_{a1} \simeq 0$, i.e. $\alpha_1 = 1$ and equation (26) simplifies to the form:

$$\eta_r = 1 + A\sqrt{c\alpha_2\alpha_3} + B_1(1 - \alpha_2)c + \alpha_2[B_2(1 - \alpha_3)c + B_3\alpha_3c] \qquad (28)$$

for which the values α_1, α_2 are easily obtainable and the above mentioned two method of solution can be applied (the nonlinear least squares method and linearisation of equation (28) to the simplified form of equation (26)).

$$y = \frac{\eta_r - 1 - A\sqrt{c_1\alpha_2\alpha_3} - B_1c(1 - \alpha_2)c}{\alpha_2\alpha_3c} = B_3 + B_2\frac{1 - \alpha_3}{\alpha_3} \qquad (29)$$

Frequently, also the relation $K_{a3} > K_{a2} \simeq 0$ and $\alpha_2 \simeq 1$ takes place. In this case only the parameters B_2 and B_3 remain unknown and the equation (26) changes its form:

$$\eta_r = 1 + A\sqrt{c\alpha} + B_2(1 - \alpha_3)c + B_3\alpha_3c$$

which can be easily rearranged to the form easily solvable by using the simple least squares method.

In the case of completely dissociated electrolytes of KA_3 type $(\alpha_1 = \alpha_2 = \alpha_3 = 1)$ equation (27) simplifies to the form:

$$\eta_r = 1 + A\sqrt{c} + B_3c$$

which can be also solved using earlier mentioned methods applicable to the completely dissociated 1-1 electrolytes.

As a recapitulation, one should claim that until now the proposed new methods of solving the Jones-Dole equation for the incompletely dissociated electrolytes (especially non-symetric ones) were no reported in the literature regarded to viscosity of electrolyte solution.

I hope that these methods will be useful in determination of the coefficients A and B of the extended Jones-Dole equation. It is especially significant, because the values of A and B coefficients reflect ion-ion and ion-solvent interaction, respectively. They are directly connected with specified ions, which sufficiently facilitates interpretation of obtained data.

REFERENCES

[1] A. B a l d, Acta Univ. Lodz., Folia Chimica, 9, 33 (1991).

[2] N. M a r t i n i u s, C. D. S i n c l a i r, C. A. V i n- c e n t, Electrochim. Acta, 22, 1183 (1977).

[3] J. C r u d d e n, G. M. D e l a n e y, D. F e a k i n s, P. J. O'R e i l l y, W. E. W a g h o r n e, K. G. L a w- r e n c e, J. Chem. Soc., Faraday Trans. I, 82, 2195, 2207 (1985).

[4] T. E r d e y-G r u z, Transport Phenomena in Aqueous Solutions, Budapest 1974, p. 128.

[5] C. W. D a v i e s, V. E. M a l p a s s, Trans. Faraday Soc., 72, 2075 (1964).

[6] C. Q u i n t a n a, M. L. L l o r e n t e, M. S a n c h e s, A. V i v o, J. Chem. Soc. Faraday Trans. I, 82, 3307 (1986).

[7] J. C. J u s t i c e, J. Chim. Phys., 65, 353 (1968).

[8] J. C. J u s t i c e, Electrochim. Acta, 18, 701 (1971).

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WPŁYW ASOCJACJI JONOWEJ NA LEPKOŚĆ ROZTWORÓW ELEKTROLITÓW

II. METODY WYZNACZANIA WSPÓŁCZYNNIKÓW RÓWNANIA JONESA-DOLE'A

Zaproponowano szereg metod rozwiązywania równań Jonesa-Dole'a dla roztworów elektrolitów niecałkowicie zdysocjowanych typu KA, KA_2, K_2A, KA_3, i K_3A (K - kation, A - anion) [1]. Rozważano różne warianty uwzględniające wartości stałych równowag jonowych. Proponowane metody mają na celu głównie poprawne wyznaczenie wartości współczynników B równania Jonesa-Dole'a i powiązania tych wartości ze ściśle określonymi jonami.