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Traceable mean activity coefficients of barium chloride in dilute aqueous solutions from $T = (273 \text{ to } 333)$ K and at $T = 298.15$ K up to the saturated solution where the molality is $1.7884 \text{ mol} \cdot \text{kg}^{-1}$

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ABSTRACT

Two new Hückel equations have been determined for the activity coefficients (γ) of $BaCl_2$ in aqueous solutions at $T = 298.15$ K. One of these equations is a two-parameter equation with parameters B (related closely to the ion-size parameter in the Debye–Hückel theory) and b_1 (the coefficient of the linear correction term in Hückel equation where $\ln(\gamma)$ is presented *vs.* the molality). It can be used up to an ionic strength ($= I_m$) of $2.0 \text{ mol} \cdot \text{kg}^{-1}$. The other is a three-parameter Hückel equation with parameters B, b_1, and b_2 (the coefficient of the quadratic correction term in extended Hückel equation), and it applies up to the saturated solution where I_m is $5.3652 \text{ mol} \cdot \text{kg}^{-1}$. The two $BaCl_2$ parameters for dilute solutions were evaluated from the isopiestic data of Robinson (1940) [4]. These new parameters were tested with all isopiestic and galvanic cell data available in the literature for this investigation. The electrochemical data measured by Tippetts and Newton using two-phase barium amalgam cells (Tippetts and Newton, 1934) [16] show that the new parameter values apply without any changes in the best case up to I_m of $3.0 \text{ mol} \cdot \text{kg}^{-1}$ at temperatures from (273 to 333) K. For more concentrated solutions at $T = 298.15$ K, new values of b_1 and b_2 for the extended Hückel equation were obtained from all points up to the saturated solution in the isopiestic set of Robinson (1945) [21]. The tests of the new parameter values were carried out with the existing electrochemical, vapor pressure, isopiestic, and solubility data available for these stronger $BaCl_2$ solutions together with the existing values for the thermodynamic properties of this salt and its hydrates. Reliable activity and osmotic coefficients for $BaCl_2$ solutions can be solved by using the new Hückel and extended Hückel equations. The values from these equations are tabulated here at rounded molalities and they were compared to the literature values.

1. Introduction

Stokes [1,2] published in year 1948 the highly authoritative tables for activity and osmotic coefficients in pure aqueous solutions of 2:1 and 1:2 electrolytes for the temperature of $T = 298.15$ K. For $BaCl_2$ solutions, the values of these quantities in the tables have been based on the previously tabulated values [3] and on the results [4] of the isopiestic measurements against KCl as the reference electrolyte by Robinson. The activity and osmotic coefficients in the tables of reference [2] start at a molality of $0.1 \text{ mol} \cdot \text{kg}^{-1}$ and continues up the saturated solution where m is about $1.8 \text{ mol} \cdot \text{kg}^{-1}$. These values were also the source of the experimental results when Pitzer and Mayorga solved the parameter values of their equation for $BaCl_2$ solutions (see references [5–7]).

In the same way as in references [8–10] for $CaCl_2$, $MgCl_2$, and $SrCl_2$ solutions, respectively, it is reported now that reliable thermodynamic quantities for solutions of $BaCl_2$ at $T = 298.15$ K can be obtained at least up to an ionic strength ($= I_m$) of $2.0 \text{ mol} \cdot \text{kg}^{-1}$ using the Hückel equation with two parameters (B and b_1) depending the electrolyte. B and b_1 for these dilute solutions were evaluated here from the data of the isopiestic measurements of Robinson [4] for KCl and $BaCl_2$ solutions, and the points where I_m for $BaCl_2$ is less than $2.34 \text{ mol} \cdot \text{kg}^{-1}$ were possible to include in the evaluation. For KCl solutions, the Hückel equation from reference [11] was used. The new Hückel equation for $BaCl_2$ solutions were additionally tested using the dilute points from the isopiestic $BaCl_2$ sets measured by Robinson and Bower against NaCl [12] and KCl [13] solutions and using those measured by Phillips *et al.* [14] against $SrCl_2$ solutions. The Hückel parameters for NaCl were taken

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from reference [11] and those for $SrCl_2$ from reference [10]. Also, cell potential difference (=cpd) data measured by Ardizzone *et al.* [15] using cells with a one-phase Ba amalgam electrode and a (Ag + AgCl) electrode at temperatures from (283.15 to 343.15) K were used in the tests. Additionally, the cpd data measured by Tippetts and Newton [16] in dilute $BaCl_2$ solutions using cells with a two-phase Ba amalgam electrode and a (Ag + AgCl) electrode from (273.15 to 318.15) K and those obtained by Lucasse [17] using concentration cells with a Ba amalgam electrode and two (Ag + AgCl) electrodes at $T = 298.15$ K were available for the tests. Finally, the new Hückel equation was tested with the freezing-point depression data of Jones [18], Hall and Harkins [19], and Gibbard and Fong [20].

It is presented, in addition, in this investigation for $T = 298.15$ K (as, for example, in reference [8] for $CaCl_2$ solutions) that the Hückel equation can be supplemented with a quadratic term in the molality and the resulting equation is useful up to the saturated ionic strength of 5.365 $\text{mol} \cdot \text{kg}^{-1}$. The coefficient multiplying the square of the molality in this term is b_2. For this supplemented Hückel equation, the parameters were estimated and tested now as follows (*i.e.*, principally in the same way as that in references [8–10]): For parameter B, the dilute-solution value was accepted. For parameters b_1 and b_2, new values for less dilute solutions were first determined from the isopiestic data of Robinson [21] for NaCl and $BaCl_2$ solutions and all of the points in this set were included in the determination. The extended Hückel equation for the former electrolyte is given in reference [11]. The validity of the parameter values determined were, additionally, evaluated with the isopiestic sets of Robinson [4], Robinson and Bower [12,13], and Phillips *et al.* [14], and all points in these sets were taken into account in the tests. The Hückel parameters for KCl and $SrCl_2$ solutions for these tests were taken from references [11] and [10], respectively. All electrochemical points from the data of Tippets and Newton [16] at $T = (288.15, 298.15, 308.15, \text{and } 318.15)$ K were also used in these evaluations as well as the vapor pressure data of Newton and Tippetts [22] at $T = 298.15$ K, and those of Bechtold and Newton [23] at $T = (298.15, 308.15, \text{and } 318.15)$ K. At $T = 298.15$ K, the solubility value of 1.7884 $\text{mol} \cdot \text{kg}^{-1}$ [16] together with the thermodynamic data for $BaCl_2$ salt and its hydrates presented in the NBS tables [24] were additionally applied in the evaluations of these new parameter values.

Similarly as in the previous studies, where solutions of uni-univalent (see references [11,25–35]) and biunivalent electrolytes [8–10] were investigated, the tests were performed here with the data obtained using real experimental techniques of various sources. This method has the advantage that the prediction error can be directly compared to the experimental error. The evaluations performed in this way confirm the good quality of the new Hückel equations. The activity coefficients of $BaCl_2$ and the osmotic coefficients and vapor pressures of water in $BaCl_2$ solutions were then tabulated using the new Hückel equations at rounded molalities. These tabulated values and the literature values were compared to each other, and the deviation between these two for activity coefficients is plotted as the cell-potential deviation for galvanic cells (as in [8–11,25–35]) and the same deviation for osmotic coefficients as the vapor pressure deviation [8–11,26–35] as functions of the molality. Similarly as for $CaCl_2$, $MgCl_2$, and $SrCl_2$ solutions [8–10], the new activity values for $BaCl_2$ solutions are traceable because all results from their estimations and tests are given in detail in the present study or in the previous studies. For the data from the isopiestic method, this is possible because traceable osmotic coefficients are reported in reference [11] for the standard reference solutions of this method required in this study (*i.e.*, for NaCl and KCl solutions).

2. Theory

Earlier [11,25–35], it was observed that the subsequent Hückel equations apply well to the mean activity coefficient (γ) and osmotic coefficient (ϕ) in aqueous solutions of many uniunivalent salts at least up to the molality of 1 $\text{mol} \cdot \text{kg}^{-1}$:

$$\ln \gamma = -\frac{\alpha |z_+ z_-| (I_m)^{1/2}}{1 + B(I_m)^{1/2}} + b_1 (m/m^o), \tag{1}$$

$$\phi = 1 - \frac{\alpha |z_+ z_-|}{B^3 I_m} \left[\left(1 + B(I_m)^{1/2}\right) - 2 \ln \left(1 + B(I_m)^{1/2}\right) - \frac{1}{1 + B(I_m)^{1/2}} \right] + \frac{1}{2} b_1 (m/m^o). \tag{2}$$

In references [8–10], in addition, it was observed that these equations apply to $CaCl_2$, $MgCl_2$, and $SrCl_2$ (2:1 electrolytes) solutions up to I_m of 1.5 $\text{mol} \cdot \text{kg}^{-1}$. In those, m is the molality, I_m is the ionic strength, z_+ is the charge number of the cation and z_- that of the anion, α is Debye–Hückel parameter (its values at the pressure of 101.325 kPa at various temperatures were taken from reference [36] and are given in table 1 of the present study), and the parameters dependent on the electrolyte are B and b_1. For a 2:1 electrolyte like $BaCl_2$, $|z_+ z_-|$ is 2 and I_m is $3m$. The osmotic coefficient of the water (label 1) is defined using the water activity (a_1) as follows

$$\ln a_1 = -\upsilon m M_1 \phi, \tag{3}$$

where M_1 is the molar mass of water (=0.018015 $\text{kg} \cdot \text{mol}^{-1}$) and now the stoichiometric number ν is 3. For the present purposes, the water activity is associated with the vapor pressure of water over the solution (p_1) and that of pure water (p_1^*) by

$$a_1 = \frac{p_1}{p_1^*}, \tag{4}$$

The values of p_1^* at various temperatures for water have been taken from reference [37] and are given in table 1. In less dilute solutions, as previously [8–11,25–35], the subsequent extended Hückel equations were now used in $BaCl_2$ solutions:

$$\ln \gamma = -\frac{2\alpha (I_m)^{1/2}}{1 + B(I_m)^{1/2}} + b_1 (m/m^o) + b_2 (m/m^o)^2, \tag{5}$$

$$\phi = 1 - \frac{2\alpha}{B^3 I_m} \left[\left(1 + B(I_m)^{1/2}\right) - 2 \ln \left(1 + B(I_m)^{1/2}\right) - \frac{1}{1 + B(I_m)^{1/2}} \right] + \frac{1}{2} b_1 (m/m^o) + \frac{2}{3} b_2 (m/m^o)^2. \tag{6}$$

TABLE 1
Debye–Hückel parameter (α)[a] and the vapor pressure of pure water (p_1^*)[b] as functions of the temperature (T).

T/K	$\alpha/(\text{mol} \cdot \text{kg}^{-1})^{-1/2}$	p_1^*/Pa
273.15	1.1293	
283.15	1.1462	
288.15	1.1552	
293.15	1.1646	
298.15	1.1744	3168.6
303.15	1.1848	
308.15	1.1956	5626.4
313.15	1.2068	
318.15	1.2186	9589.8
323.15	1.2308	
328.15	1.2436	
333.15	1.2568	
343.15	1.2846	

[a] Given by Archer and Wang [36].
[b] Given by Kell [37].