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Manuscript received September 21, 1972; revision received and accepted April 5, 1972.

Activity Coefficients—Aqueous Solutions of Polybasic Acids and Their Salts

HERMAN P. MEISSNER
and
NIKOLAOS A. PEPPAS

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

A method of predicting activity coefficients of polybasic acids and their salts in strong aqueous solutions is presented. Application of the calculation of decomposition pressures of SO_2 over sodium sulfite-bisulfite systems and of CO_2 over carbonate-bicarbonate systems is illustrated.

SCOPE

Correlations have recently been presented (Meissner and Tester, 1972; Meissner et al., 1972; Meissner and Kusik, 1972) whereby the mean ionic activity coefficients of many types of electrolytes, notably neutral salts such as NaCl, $AlCl_3$, etc., can be estimated in both pure and mixed aqueous solutions at temperatures of from 0 to 150°C, and at concentrations up to saturation. It is desirable to extend these simple correlations to more complex ionic soluions.

CONCLUSIONS AND SIGNIFICANCE

It is demonstrated that one may predict the activity coefficients of (1) the strong polybasic acids, namely H_2SO_4, H_3AsO_4, and H_3PO_4, (2) the acid salts of these strong polybasic acids such as $NaHSO_4$, K_2HPO_4, etc., and (3) the acid salts of the weak polybasic acids such as $NaHCO_3$, $KHSO_3$, sodium hydrogen malonate, potassium hydrogen succinate, etc. Such activity coefficients can be employed in the calculation of chemical equilibria, as when the dissociation pressures of CO_2 over aqueous carbonate-bicarbonate solutions and of SO_2 over sulfite-bisulfite solutions are approximated.

STRONG ACIDS

For strong electrolytes, isotherms of log $\Gamma°$ versus concentration expressed in ionic strength units fall into the curve family of Figure 1 at all temperatures from the freezing point to about 150°C (Meissner et al., 1972). Since there is little curve cross-over, location of one point on Figure 1 for an electrolyte at any temperature serves to locate the entire isotherm, after which the isotherms at other temperatures are readily located, as discussed later.

Strong monobasic acids like HCl, HBr, HI, HNO_3, $HClO_4$, etc. are all members of this generalized curve family. The strong polybasic acids are likewise found to be members, providing they are properly classified in terms of their ion charges z_1 and z_2. That is, the magnitude of these charges for polybasic acids is not as obvious as for the neutral salts like NaCl or K_2SO_4, which are extensively dissociated in aqueous solution. Thus H_3PO_4 could be viewed either as a 1:1 electrolyte dissociating to H^+ and $H_2PO_4^-$, as a 1:2 electrolyte dissociating to $2H^+$ and HPO_4^{2-}, or as a 1:3 electrolyte dissociating as $3H^+$ and PO_4^{3-}. While a self-consistent set of Γ° versus μ values can be calculated for any strong polybasic acid for each of these assumptions, it is convenient to use z_1 and z_2 values for which the resultant curve of log Γ° versus μ comes closest to being a member of the curve family of Figure 1.

The activity coefficients at 100°C for the two strong polybasic acids H_3PO_4 and H_3AsO_4 treated at 1:1 electrolytes, calculated from vapor pressure data (Smithsonian Tables, 1954) by the method of Kusik and Meissner (1973), are presented as dashed curves on Figure 2. Inspection shows that these dashed curves fit well into the generalized curve family represented by the solid curves of Figure 2. Recalculations of the experimental data when treating these acids as 1:2 or as 1:3 electrolytes result in curves which do not fit into the generalized curve family. The finding that these polybasic acids fit best as 1:1 electrolytes presumably reflects the large magnitudes of their first dissociation constants and the small magnitudes of their second (and third) dissociation constants. Thus a solution of H_3PO_4 acts as a 1:1 electrolyte since it contains primarily H^+ and $H_2PO_4^-$ ions, with only very small amounts of HPO_4^{2-} and PO_4^{3-} ions present. With the exception of sulfuric acid, polybasic acids like arsenic acid behave similarly.

Sulfuric acid, unlike most polybasic acids, shows a relatively large second dissociation constant as well as a large first dissociation constant. It is consequently not surprising to find that H_2SO_4 fits into the generalized curve family as a 1:2 electrolyte as curve 5 of Figure 2 [data from Harned and Owen (1958) based upon vapor pressures]. The generalization which appears to apply to the strong polybasic acids therefore is as follows: strong polybasic acids with small second (and third) dissociation constants fit into the generalized curve family best as 1:1 electrolytes, while dibasic acids with large first and second dissociation constants fit as 1:2 electrolytes.

EFFECT OF TEMPERATURE

As pointed out by Meissner et al. (1972), electrolyte isotherms at all temperatures fall into the generalized curve family of Figure 1, but an electrolyte's isotherm at any one temperature usually does not coincide with that at another temperature. Only those points which lie on the dashed reference isotherm on Figures 1 and 2, designated by *Ref.* are unaffected by temperature change, and for these points, $(\partial \log \Gamma^\circ/\partial T)_\mu$ is obviously zero.

The effect of temperature change upon a known value of log Γ° at any given ionic strength can be evaluated by the procedure discussed by Meissner et al. (1972). A simple and convenient approximation of this procedure involves use of the following equation which applies at any constant value of μ:

$$\log \Gamma^\circ{}_T = (1.125 - 0.005T) \log \Gamma^\circ{}_{25^\circ C} - (0.125 - 0.005T) \log \Gamma^\circ{}_{\text{ref}} \quad (1)$$

where log $\Gamma^\circ{}_{\text{ref}}$ is obtained either from the dotted line on Figure 1, or from the following equation for this line:

$$\log \Gamma^\circ{}_{\text{ref}} = -\frac{0.41\mu^{0.5}}{1+\mu^{0.5}} + 0.039\mu^{0.92} \quad (2)$$

Inspection of Equation (1) shows that, as expected, log $\Gamma^\circ{}_T$ and log $\Gamma^\circ{}_{25^\circ C}$ are identical when log $\Gamma^\circ{}_{25^\circ C}$ for an

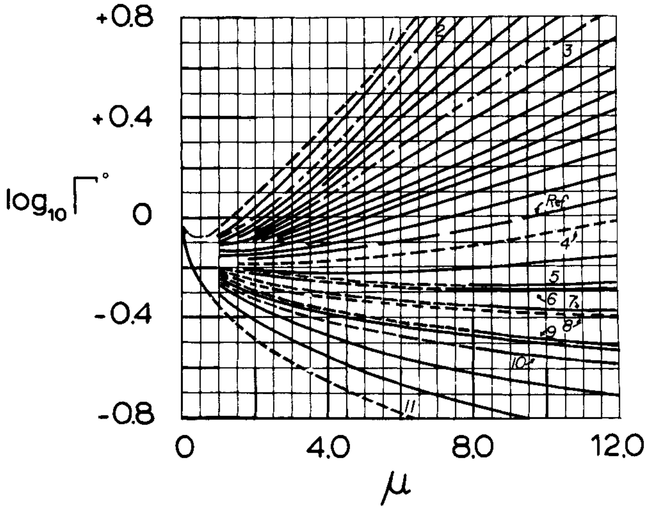

Fig. 1. Generalized isotherms: reduced ionic activity coefficients versus μ, the ionic strength. For all points on the dotted reference line, (∂ log Γ°/∂T) at constant μ is zero.

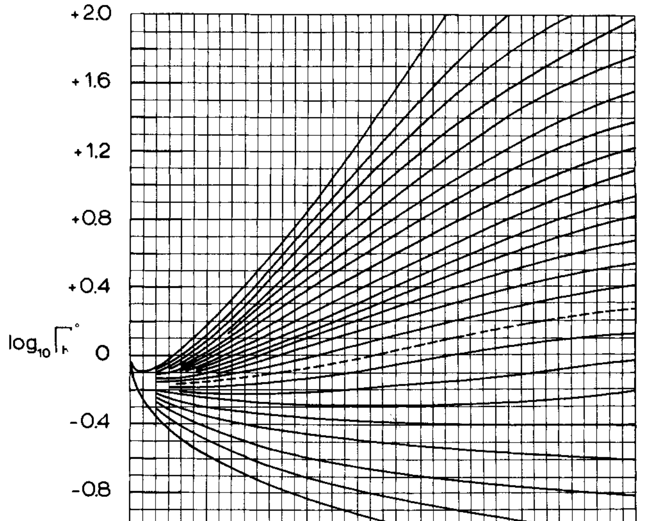

Fig. 2. Activity coefficients of acids and salts: The lengths of these dotted curves, numbered as follows, indicate the concentration ranges over which published data are available: 1-HBr as 1:1 electrolyte at 25°C, 2-HCl as 1:1 at 25°C, 3-sodium acetate as 1:1 at 25°C, 4-$NaHCO_3$ as 1:1 at 100°C, 5-H_2SO_4 as 1:2 at 100°C, 6-K_3AsO_4 and K_3PO_4 as 1:3 electrolytes and disodium fumarate as 1:2, all at 25°C; 7-K_2HAsO_4 as 1:2 at 25°C, 8-$NaHSO_4$ as 1:2 at 100°C, also both Na_2CO_3 and disodium malonate as 1:2 at 25°C, 9-K_2HPO_4 as 1:2 at 25°C and potassium hydrogen succinate as 1:1 at 25°C, 10-potassium hydrogen malonate as 1:1 at 25°C and 11-both KH_2AsO_4 and KH_2PO_4 as 1:1 at 25°C. On the dashed curve marked *Ref*, (∂ log Γ/∂T) at constant concentration is zero at all points.

electrolyte falls on the dotted reference line of Figure 1.

Use of Equation (1) can be illustrated by predicting log Γ° for HCl at 50°C when μ is 15, knowing that at this ionic strength the experimental value of log Γ° at 25°C is 1.533. From the dotted line of Figure 1 [or from Equation (2)], log Γ°_{ref} is 0.165 when μ is 15. Substituting into Equation (1), log Γ° for HCl at 50°C when μ is 15 is found to be 1.36, which checks well with the experimental value of 1.31. Equation (1) applies equally well to the polybasic acids and their salts.

POLYBASIC ACID SALTS

Because of the small magnitude of the second and third dissociation constants of most strong (and weak) polybasic acids, solutions of the acid salts of these acids again contain relatively small concentrations of hydrogen ions. That is, a primary salt like KH_2PO_4 dissociates to K^+ and $H_2PO_4^-$ *ions*, but the $H_2PO_4^-$ *ion in turn* ionized only to a very limited extent to HPO_4^{2-} and to PO_4^{3-}, etc. Consequently, it is not surprising to find that the primary alkali salts of H_3PO_4 and H_3AsO_4 act as 1:1 salts with respect to the curve family of Figure 1, the secondary salts act as 1:2 electrolytes, and the ternary as 1:3 electrolytes. When so treated, curves on Figure 2 for the various potassium salts of these acids (Scatchard and Breckenridge, 1954) fall into the generalized curve family. Other salts of these acids, namely their sodium and ammonium salts, show similar behavior. Further illustrations are the curves on Figure 2 for $NaHCO_3$ treated as a 1:1 electrolyte (from vapor pressure data in the Smithsonian Tables, 1954) and for Na_2CO_3 treated as a 1:2 electrolyte (Harned and Owen, 1958). Similarly, the limited data available for the salts of organic acids with two carboxyl groups fall into this generalized curve family, as shown by the following on Figure 2: the monosodium salts of succinic and malonic acids treated as 1:1 electrolytes (Stokes, 1948), and the disodium salts of fumaric and maleic acids treated as 1:2 electrolytes (Robinson, Smith, and Smith, 1942). Again as expected, bisulfates act not as 1:1 but as 1:2 electrolytes, presumably reflecting the large second dissociation constant of H_2SO_4 This is illustrated on Figure 2 for the typical case of $NaHSO_4$ plotted as a 1:2 electrolyte (data from Smith and Robinson, 1942).

Since the generalized curve family of Figure 1 is only for strong electrolytes, it does not apply to the weak acids and bases. As already shown, the salts of such weak inorganic acids, being strong electrolytes, fall into this curve family. The salts of the lower fatty acids also fall into this family, as shown by the curve on Figure 2 for sodium acetate (Smith and Robinson, 1942). However, salts of the longer-chain fatty acids, such as propionic butyric, etc., show increasing deviations from Figure 1.

APPLICATION

The published data points for the activity coefficients and vapor pressures versus concentration for various electrolytes, on which the dotted curves of Figure 2 are based, are themselves from smoothed curves. No attempt has been made here, therefore, to present these original data points on Figure 2. The success attained in fitting the data for the acids and acid salts of Figure 2 into the curves of Figure 1 is similar to that for other 1:1, 1:2, 2:1, etc., electrolytes, as discussed by Meissner and Tester (1972). Applications of these relations is now illustrated by estimating the dissociation pressures of CO_2 and SO_2 over carbonate-bicarbonate solutions and over sulfite-bisulfite solutions respectively. For these calculations, relations published elsewhere are required and briefly reviewed here:

1. The activity of an electrolyte 12, present either alone in pure solution or with other electrolytes in mixed solution, is related to the ion molalities m_1 and m_2 and to its mean ionic activity coefficient γ_{12} as follows (Robinson and Stokes, 1955):

For a 1:1 electrolyte, activity $= m_1 m_2(\gamma^2{}_{12})$
For a 2:1 electrolyte, activity $= m_1 m_2{}^2(\gamma^3{}_{12})$
For a 1:2 electrolyte, activity $= m_1{}^2 m_2(\gamma^3{}_{12})$
For a 2:2 electrolyte, activity $= m_1 m_2(\gamma^2{}_{12})$, etc.

It will be remembered that in pure solution, m_1 and m_2 are stoichiometrically related to the electrolyte's molality m_{12}. Thus for pure NaCl, m_{12}, m_1, and m_2 are all equal. For pure Na_2SO_4, m_1 equals $2m_{12}$, but m_2 equals m_{12}, etc.

2. The relations between $\Gamma^\circ{}_{12}$, the reduced ionic activity coefficient of electrolyte 12 in a mixed solution, and the ionic strength fractions X and Y were presented by Meissner and Kusik (1972). For a system of two electrolytes 12 and 14 having a common anion:

$$\log \Gamma_{12} = 1/2[X_1 \log \Gamma^\circ{}_{12} + Y_2 \log \Gamma^\circ{}_{12} + Y_4 \log \Gamma^\circ{}_{14}] \tag{4}$$

This equation is readily extended to solutions containing additional ions.

3. For a solution containing electrolytes 12 and 14, the approximate relation between $(a_w)_{\text{mix}}$, the activity of water in a mixed solution, and $(a_w{}^\circ)_{12}$ and $(a^\circ{}_w)_{14}$, namely the water activities over pure solutions of the indicated components at the same total ionic strength and temperatures of the mixed solution, is as follows:

$$\log(a_w)_{\text{mix}} = X_1 Y_2 \log(a_w{}^\circ)_{12} + X_1 Y_4 \log(a^\circ{}_w)_{14} \tag{5}$$

This equation is again readily expanded for solutions containing more than three ions (Meissner and Kusik, 1973).

DISSOCIATION PRESSURES

Carbonate-Bicarbonate Solutions. The dissociation pressure of CO_2 over a solution 0.8 molal in $NaHCO_3$ and 0.1 molal in Na_2CO_3 at 65°C is 0.167 atm. (Mai and Babb, 1955). μ_a, μ_c, and μ_T are 0.6, 0.5, and 1.1, making X_{Na^+}, $Y_{HCO_3^-}$, and $Y_{CO_3{}^{2-}}$ respectively 1.0, 0.67, and 0.34. The primarly reaction occurring is

$$2NaHCO_3(aq) = CO_2(g) + H_2O(l) + Na_2CO_3(aq); \qquad \log K_{25^\circ C} = -2.529 \tag{6}$$

with the following equilibrium constant:

$$K = P_{CO_2} - (a_w)_{\text{mix}} \cdot \frac{\{\gamma_{Na_2CO_3}\}^3\{m_{CO_3{}^{2-}}\}}{\{\gamma_{NaHCO_3^-}\}^4\{m_{HCO_3^-}\}^2} \tag{7}$$

The standard state of each salt is of course in its pure hypothetical solution having a mean ionic molality of unity, in which the salt's activity is unity. Assuming ΔH for reaction (6) to be constant at +6.36 Kcals (all values of ΔH 65°C and K at 25°C from Rossini, 1952), then by the vant Hoff equation K is 0.011. Log $\Gamma_{25^\circ C}$ values for Na_2CO_3 and NaOH at 25°C and an ionic strength of 1.1 are obtained from Figure 2, and extrapolated to 65°C with Equation (1). The resultant values of log $\Gamma^\circ{}_{65^\circ C}$ and the associated values of $(a^\circ)_w$ as read from Figure 2 are presented below along with the associated values of log $\Gamma_{65^\circ C}$ obtained from Equation (4):

$\mu_T = 1.1$; $T = 65°C$

	$\log \Gamma°$	$\log (a°)_w$	From Equation (4) $\log \Gamma$	γ
$NaHCO_3$	−0.201	0.015	0.199	0.632
Na_2CO_3	−0.191	0.007	0.194	0.41

The value of $(a_w)_{mix}$ from Equation (5) is 0.98. Substituting into Equation (7), $^{P}CO_2$ is found to be 0.166 in good agreement with experiment.

Sulfite-Bisulfite Solutions. The success obtained above in calculating dissociation pressures over the carbonate-bicarbonate solutions is not always equalled because of errors encountered in using relations like Equation (7). That is, values of a_{mix} and γ may themselves contain experimental errors or may not fall perfectly into the generalized curve family of Figure 1. Such errors are magnified by the fact that terms in Equation (7) involving a and γ are raised to powers. For example, consider an aqueous solution of $NaHSO_3$ and Na_2SO_3, which generates SO_2 as follows:

$$2NaHSO_3(aq) = Na_2SO_3(aq) + SO_2(g) + H_2O(l), \quad K_{25°C} = 3260 \qquad (9)$$

The equilibrium constant expression here is similar to that of Equation (7). Dissociation pressures over this system were measured at various temperatures by Johnstone et al. (1938). Morgan (1960, 1961) stated that he could make only qualitative comparisons between these data and his own experimentally determined activity coefficients for Na_2SO_3 and $NaHSO_3$ solutions at 25°C. Similarly, we find that the equilibrium constants calculated for Equation (9) from the data of Johnstone and the activity coefficients of Morgan are severalfold smaller than those based upon the data of Rossini. However, better agreement is obtained here by an arbitrary modification of the activity coefficient values for $NaHSO_3$. That is, we assume $NaHSO_3$ to be a 1:1 electrolyte whose curve on Figure 1 would have a value for $\log \Gamma°$ at 25°C of −0.572 when μ is 4.8. We retain Morgan's activity coefficient values for Na_2SO_3, treating it as a 1:2 electrolyte for which $\log \Gamma°$ at 25°C is −0.35 when μ is 4.8. Extrapolating with Equation (1) and recognizing that $\log \Gamma°_{ref}$ is −0.12 from Figure 1 when μ is 4.8, then values of $\Gamma°$ for $NaHSO_3$ and Na_2SO_3 at this ionic strength are respectively 0.35 and 0.30 at 90°C. Using the corresponding curves on Figure 1 to predict γ at various ionic strengths, K values calculated from equation (7) for Johnstone's various data points at 90°C average 1900 ± 30%, versus the value of 1890 as extrapolated from the data at 25°C for ΔH and K from Rossini (1952) using the vant' Hoff equation.

NOTATION

a = activity of water where $(a_w°)_{12}$ refers to pure solutions containing only electrolyte 12, while $(a_w)_{mix}$ refers to mixed solutions containing more than one electrolyte

K = equilibrium constant

m = molality in gram moles per 1000 grams water, $m°$ referring to pure solutions of a single electrolyte, m referring to a mixed solution containing more than one electrolyte. Ions or electrolytes are identified by subscript, hence m_1, m_2, and m_{12} are respectively molalities of cation 1, anion 2 and electrolyte 12.

X = cationic fraction, as in μ_1/μ_c, μ_3/μ_c, etc.

Y = anionic fraction, as in μ_2/μ_a, μ_4/μ_a, etc.

z = number of unit charges in the ion indicated by subscript. Thus in a mixed solution containing Na^+, NO_3^-, Al^{3+}, HPO_4^{2-}, arbitrarily called ions 1, 2, 3, and 4, z_1 is 1, z_2 is 1, z_3 is 3, and z_4 is 2.

ν = moles of ions formed upon complete dissociation of one mole of electrolyte. Thus ν_{12} counts the total ions, would be 2 for NaCl and 5 for $Al_2(SO_4)_3$. Similarly, ν_1 is the moles of the indicated cation, ν_2 is moles of the indicated anion, all per mole of electrolyte. In $Al_2(SO_4)_3$, ν_1 is 2 for the aluminum ions, while ν_2 is 3 for the sulfate ions.

μ = ionic strength, namely $1/2(m_1z_1^2 + m_2z_2^2 + m_3z_3^2 + \ldots)$. The cationic strength μ_c is $1/2(m_1z_1^2 + m_3z_3^2 + m_5z_5^2 \ldots)$, the anionic strength μ_a is $1/2(m_2z_2^2 + m_4z_4^2 + m_6z_6^2 \ldots)$ where μ equals $(\mu_a + \mu_c)$.

Subscripts

The cations in a system are designated as 1, 3, 5, etc., the anions as 2, 4, 6, etc.

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Manuscript received October 6, 1972; revision received February 14 and accepted February 16, 1973.