

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF SOUTH CAROLINA]

Activity Coefficients of *p*-Toluenesulfonic Acid and Sodium *p*-Toluenesulfonate in Mixed Solutions

BY O. D. BONNER AND V. F. HOLLAND

RECEIVED JUNE 27, 1955

Activity coefficients of *p*-toluenesulfonic acid and sodium *p*-toluenesulfonate at 25° in mixtures of the two electrolytes have been calculated from isopiestic data. These electrolytes do not obey Harned's rule.

Introduction

There have been few investigations of the behavior of electrolytes in mixed solutions until recent years. Harned and Owen¹ have been able to calculate the activity coefficients of both electrolytes in mixtures if the logarithm of the activity coefficient of each electrolyte varies linearly with its concentration in mixtures of constant total molality. This restriction limits the use of their treatment to certain pairs of strong electrolytes. Moderate and weak electrolytes would not be expected to obey Harned's rule. Recently McKay and Perring² have derived equations which allow the calculation of the activity coefficients of both electrolytes in a mixed solution from measurements of water activities. Since neither calculated quantity is determined by direct experiment it is to be expected that any experimental error in the determination of the water activity will be magnified in the calculation of the activity coefficients. This magnification of errors is increased by the multitude of mathematical calculations which are necessary to convert the data to its final form. Nevertheless, this treatment permits investigations of three component systems which were not possible in the past.

McKay's equation for the calculation of the activity coefficient of solute 1 is

$$0.018\nu_1 \ln \left(\frac{m\gamma_1}{M\Gamma_1} \right) = k_1 \int_0^{\ln a_w} \left\{ -\frac{1}{m^2} \left(\frac{\partial m}{\partial \ln X_2} \right)_{a_w} - \frac{1}{m} + \frac{1}{M} \right\} d \ln a_w \quad (1)$$

where $m = k_1 m_1 + k_2 m_2$, $X_1 = k_1 m_1 / m$ and M and Γ are the molality and activity coefficients of solute 1 in a solution containing only solute 1 which is isopiestic with the mixed solution. The quantity m may be the ionic strength if k_1 and k_2 are suitably chosen. Sometimes it is inconvenient to use a solution of pure solute 1 as a reference solution. Equation 1 may be generalized so that a solution containing a third solute of the same valence type, such as lithium or sodium chloride or sulfuric acid, may be used.

$$0.018 \nu_1 \ln \left(\frac{m\gamma_1}{m_r\gamma_r} \right) = k_1 \int_0^{\ln a_w} \left\{ -\frac{1}{m^2} \left(\frac{\partial m}{\partial \ln X_2} \right)_{a_w} - \frac{1}{m} + \frac{1}{m_r} \right\} d \ln a_w \quad (2)$$

If this treatment is limited to uni-univalent electrolyte mixtures we find that $\nu_1 = \nu_2$, $k_1 = k_2 = 1$ and m is the ionic strength. Since this treatment is ideally

(1) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 461.

(2) H. A. C. McKay and J. K. Perring, *Trans. Faraday Soc.*, **362**, 163 (1953).

adapted to isopiestic experiments, it is also convenient to change the variable from $\ln a_w$ to $(m\varphi)$, the product of the molality and the practical osmotic coefficient, since for isopiestic solutions of uni-univalent electrolytes $m_1\varphi_1 = m_2\varphi_2$. Upon making these substitutions equation 2 reduces to

$$\ln \left(\frac{m\gamma_1}{m_r\gamma_r} \right) = \int_0^{m\varphi} \left\{ \frac{1}{m^2} \left(\frac{\partial m}{\partial \ln X_2} \right)_{m\varphi} + \frac{1}{m} - \frac{1}{m_r} \right\} d(m\varphi) \quad (3)$$

If the molality ratio m_r/m is defined as R , then equation 3 takes the form

$$\ln \gamma_1 = \ln R + \ln \gamma_r + \int_0^{m\varphi} \left\{ \frac{1}{m^2} \left(\frac{\partial m}{\partial \ln X_2} \right)_{m\varphi} + \frac{1}{m} - \frac{1}{m_r} \right\} d(m\varphi) \quad (4)$$

An alternate form which is more convenient for calculations is

$$\ln \gamma_1 = \ln R + \ln \gamma_r + \int_0^{m\varphi} \left\{ X_2 \left(\frac{\partial \frac{1}{m}}{\partial X_1} \right)_{m\varphi} + \frac{R-1}{m_r} \right\} d(m\varphi) \quad (5)$$

A similar equation for the calculation of the activity coefficient of solute 2 is

$$\ln \gamma_2 = \ln R + \ln \gamma_r + \int_0^{m\varphi} \left\{ X_1 \left(\frac{\partial \frac{1}{m}}{\partial X_2} \right)_{m\varphi} + \frac{R-1}{m_r} \right\} d(m\varphi) \quad (6)$$

A more accurate and convenient method of obtaining $\ln \gamma_2$ however is to calculate a value of $\ln(\gamma_1/\gamma_2)$ and obtain $\ln \gamma_2$ as the difference, $\ln \gamma_1 - \ln(\gamma_1/\gamma_2)$. The subtraction of equation 5-6 yields

$$\ln \frac{\gamma_1}{\gamma_2} = \int_0^{m\varphi} \left\{ X_2 \left(\frac{\partial \frac{1}{m}}{\partial X_1} \right) - X_1 \left(\frac{\partial \frac{1}{m}}{\partial X_2} \right) \right\} d(m\varphi) \quad (7)$$

Utilizing the relationship $dX_2 = -dX_1$, one may obtain the simple equation

$$\ln \frac{\gamma_1}{\gamma_2} = \int_0^{m\varphi} \left(\frac{\partial \frac{1}{m}}{\partial X_1} \right)_{m\varphi} d(m\varphi) \quad (8)$$

Results and Discussion

Mixed solutions of *p*-toluenesulfonic acid and sodium *p*-toluenesulfonate containing 0.000, 0.401, 0.614, 0.800, 0.889 and 1.000 mole fraction of sodium *p*-toluenesulfonate were isopiastically compared with solutions of lithium chloride over the water activity range $m\varphi = 0$ to $m\varphi = 3.0$. Lithium chloride was chosen as the reference electrolyte in preference to sodium or potassium chloride because the behavior of $R = m_r/m$ in dilute solutions allowed more certain extrapolation to infinite dilution. Plots of R vs. $(m\varphi)$ for each solution yielded values of $1/m$ at

interpolated values of $m\phi = 0.0, 0.1, 0.2$, etc. The slope ($\partial 1/m \partial X_{HTol}$) was measured at $X_{HTol} = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ for each value of $m\phi$. These data allowed the calculations of $\ln(\gamma_1/\gamma_2)$ from equation 8. $\ln \gamma_1$ was next obtained from equation 5. Values of γ_1 and γ_2 as a function of m and X_{HTol} were next calculated and are presented in Tables I and II.

TABLE I

ACTIVITY COEFFICIENTS OF <i>p</i> -TOLUENESULFONIC ACID						
$m = X_{acid}$	0.0	0.2	0.4	0.6	0.8	1.0
0.1	0.775	0.769	0.762	0.760	0.759	0.759
.2	.740	.723	.713	.710	.706	.703
.3	.720	.697	.679	.668	.662	.660
.4	.706	.680	.655	.642	.635	.630
.5	.697	.662	.633	.620	.612	.608
.6	.690	.650	.617	.601	.593	.589
.7	.684	.640	.602	.586	.578	.573
.8	.678	.630	.590	.574	.565	.559
.9	.671	.620	.576	.562	.553	.546
1.0	.666	.610	.563	.550	.542	.535
1.2	.653	.593	.541	.527	.520	.515
1.4	.642	.576	.521	.509	.502	.498
1.6	.630	.560	.503	.493	.485	.483
1.8	.620	.544	.487	.478	.471	.469
2.0	.613	.530	.472	.464	.459	.459
2.5	.597	.508	.446	.440	.438	.439
3.0	.589	.490	.428	.423	.423	.427
3.5	.585	.478	.417	.417	.419	.425

It was to be expected that these mixed solutions would exhibit unusual behavior because of the behavior of solutions of the two pure components. It has been found,³ for example, that the osmotic coefficient of the sodium salt is greater than that of the acid in relatively dilute solutions ($m < 1.4$) and less than that of the acid in more concentrated solutions. In dilute mixed solutions $1/m$ initially increases with increasing percentages of acid at constant water activity, reaches a maximum at $X_{acid} \approx$

(3) O. D. Bonner, G. D. Easterling, D. L. West and V. F. Holland, *THIS JOURNAL*, **77**, 242 (1955).

TABLE II

ACTIVITY COEFFICIENTS OF SODIUM <i>p</i> -TOLUENESULFONATE						
$m = X_{acid}$	0.0	0.2	0.4	0.6	0.8	1.0
0.1	0.765	0.766	0.767	0.767	0.768	0.768
.2	.709	.718	.724	.726	.729	.731
.3	.674	.685	.690	.695	.698	.699
.4	.648	.659	.665	.669	.671	.673
.5	.627	.638	.645	.651	.654	.656
.6	.609	.623	.631	.636	.640	.642
.7	.593	.608	.618	.623	.629	.631
.8	.579	.595	.606	.612	.618	.621
.9	.566	.583	.595	.603	.608	.612
1.0	.554	.576	.584	.594	.600	.604
1.2	.532	.548	.563	.575	.584	.589
1.4	.511	.528	.543	.557	.568	.574
1.6	.493	.508	.524	.540	.553	.560
1.8	.476	.492	.509	.525	.539	.546
2.0	.460	.477	.495	.511	.526	.534
2.5	.427	.446	.465	.482	.498	.508
3.0	.402	.422	.442	.462	.479	.490
3.5	.383	.405	.429	.450	.469	.482

0.3, and then decreases. In concentrated solutions $1/m$ increases regularly with increasing percentages of acid at constant water activity. This behavior results in positive values of $\ln(\gamma_{acid}/\gamma_{salt})$ for solutions containing large molar fractions of salt and negative values for this quantity for solutions containing large molar fractions of acid over the concentration range 0–3.5 m .

The variation of γ_{acid} with composition at constant ionic strength is also of interest. In dilute solutions this activity coefficient decreases with increasing acid concentration. In concentrated solutions the activity coefficient has a minimum value for solutions of intermediate composition and is higher in both pure solutions.

It may be observed that neither solute obeys, Harned's rule as to the linear variation of the logarithm of the activity coefficient with composition at constant total molality.

COLUMBIA, S. C.

[CONTRIBUTION NO. 685 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Physical Chemical Studies of Solutions in Anhydrous Ethylenediamine. II. Conductances and Viscosities of Solutions of Mercuric Bromide, Iodide and Cyanide

By JOHN PEACOCK,^{1a} F. C. SCHMIDT,^{1b} R. E. DAVIS AND W. B. SCHAAP

RECEIVED APRIL 20, 1955

The solubilities of mercuric bromide, iodide and cyanide in ethylenediamine at 25° have been found to be approximately 26, 300 and 113 g./100 g. solvent (0.61, 4.18 and 3.25 M), respectively. Conductances of solutions of these salts have been measured at 25° over the available range of concentrations. The plots of equivalent conductance against concentration for HgI₂ and Hg(CN)₂ show minima and maxima. The plot for HgBr₂ shows only a minimum since the more concentrated solutions proved to be unstable and were not suitable for conductance measurements. The maxima in the conductance curves are probably due to the formation of triple ions or, perhaps, to formation of complex ions of HgX₄²⁻ (X = Br⁻, I⁻ or CN⁻) at moderate concentrations followed by a rapid drop in conductance at higher concentrations due to the large increase in viscosity observed in this region. The exceptionally high solubility of the iodide is typical of the behavior of iodides in ethylenediamine and other amine solvents. It is tentatively suggested that this is due to the solvation of the iodide through the expansion of the outer valency shell of the iodine.

Introduction

During an investigation of the solubility of certain salts in ethylenediamine,² it was found that

(1) (a) Post-Doctoral Fellow, 1953–1954. (b) Address correspondence to F.C.S.

(2) B. B. Hibbard and F. C. Schmidt, *THIS JOURNAL*, **77**, 225 (1955).

while mercuric chloride is only slightly soluble,³ and reacts with the solvent, mercuric iodide is exceedingly soluble, dissolving with the evolution of considerable heat to form yellow, viscous, conducting solutions, the color of which deepens with increasing

(3) H. S. Isbin and K. A. Kobe, *ibid.*, **67**, 464 (1945).