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ACTIVITY COEFFICIENTS OF BIPOLAR ELECTROLYTES. SILVER SUCCINATE AND SEBACATE IN AQUEOUS SODIUM NITRATE[1]

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Activity coefficients of silver succinate and sebacate in aqueous sodium nitrate were determined by a solubility method. The silver ion concentration was measured potentiometrically in solutions of various ionic strengths using an empirical calibration equation. A simple, approximate theoretical model for these "bipolar" ions is observed to be in good agreement with results inferred from the electrostatic contribution to the activity coefficients. It treats a bipolar ion as two point charges separated by a fixed distance in the solvent. Its applicability to zwitterions is also considered. These studies are used to discuss the interaction of certain activated complexes of chemical reactions with their ionic atmospheres. Studies of bipolar ions also provide information about nearest neighbor interaction in polyelectrolytes.

Introduction

The electrostatic interaction between two charges attached to the same molecule in various ionic media enters into several problems. These include the nearest neighbor repulsion of ionized groups in polyelectrolytes[2] and the activity coefficients of certain activated complexes in chemical reactions. In the latter case, for example, it is usually assumed[3] that the activated complex interacts with the ionic medium in the same way as a single localized charge, even when it may consist of essentially two charges separated by a fixed distance.

Interest in these problems prompted the present investigation of the activity coefficients of salts containing dicarboxylate ions. The simplest such system theoretically is one which is dilute in dicarboxylate ions and in which the latter interact primarily with those of a 1–1 electrolyte. In this study the activity coefficients of slightly soluble silver succinate and sebacate in aqueous sodium nitrate were measured by a solubility method. The comparison of the activity coefficients of two salts differing in their hydrocarbon chain length permits the approximate cancellation of certain non-electrostatic factors in the interpretation of the results.

It seems appropriate to term molecules containing two separate charges "bipolar ions." Examples of this class include dipolar ions (amino acids in the zwitterion form) and "bolaform" electrolytes.[4]

Experimental

Procedure.—The solubility of the silver salts in aqueous sodium nitrate at 24.8° was determined by a potentiometric measurement of the silver ion concentration. An empirical calibration equation was first obtained using solutions containing known concentrations of silver and sodium nitrate. The electrochemical cell employed in the calibration and in the solubility determination contained a saturated sodium nitrate–agar salt bridge and is represented by the expression

$$\mathrm{Hg,Hg_2Cl_2\ (s)\|KCl\ (satd.)\|NaNO_3\ (aq.\ satd.)}\ \Big|^{\text{exptl.}}_{\text{soln.}}\Big|\ \mathrm{AgCl(s),Ag}$$

A Leeds and Northrup Type K-2 potentiometer was employed, and the cell was thermostated at 24.80°. E.m.f. readings were made on the calibration solutions which varied from 1.2×10^{-4} to 1.5×10^{-3} m $AgNO_3$ and from 0.05 to 2.5 m $NaNO_3$. E.m.f. readings were then made on filtered solutions previously saturated with a silver dicarboxylate at 24.8° and containing known concentrations of sodium

(1) Abstracted in part from a dissertation submitted by Frank R. Meeks in partial fulfillment for the degree of Doctor of Philosophy, Polytechnic Institute of Brooklyn, June 1956.

(2) R. A. Marcus, This Journal, 58, 621 (1954); S. Lifson, *J. Chem. Phys.*, 26, 727 (1957); 29, 89 (1958) and references cited therein.

(3) *Cf.* S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

(4) R. M. Fuoss and D. Edelson, *J. Am. Chem. Soc.*, 73, 269 (1951)

nitrate. The empirical equation was then used to calculate the silver ion concentration.

Reagents.—Sebacic and succinic acids (Eastman Kodak) were purified by conversion to the disodium salts in concentrated aqueous solution and treatment with decolorizing carbon while boiling, followed by suction filtration and treatment with mineral acid to regenerate the organic acid. This was followed by four recrystallizations from hot distilled water, vacuum drying and a melting point check. The silver salts were generated by titration of the sodium salt of the acid with Mallinckrodt Analytical Reagent silver nitrate. The salts were filtered, washed with a little water, dried in a vacuum desiccator and stored over phosphorus pentoxide.

Sodium nitrate (Mallinckrodt A.R.) was recrystallized four times from hot water. Unrecrystallized sodium nitrate became slightly milky in the presence of 0.001 m $AgNO_3$ if the sodium nitrate exceeded 0.5 m. However, even after one recrystallization no milkiness occurred. A colorimetric test[5] for chloride on recrystallized sodium nitrate also proved negative. Sodium nitrate was selected as a suitable 1–1 electrolyte both because of its solubility and because of its relative freedom from contamination with halide ions. Care was taken to ensure low CO_2 content to minimize possible hydrolysis of the dicarboxylate salts. Direct titration of these solutions of sodium nitrate in water using phenolphthalein then showed that hydrolysis could be ignored (being of the order of 1%).

Results

The mean molal ion activity coefficient of the silver dicarboxylate, $\nu_\pm$, in a solution in equilibrium with the solid can be expressed in terms of the measured silver ion molality, m_{Ag^+}, and in terms of the latter's value at zero ionic strength, $m^0_{Ag^+}$, according to the thermodynamic expression

$$-\log \gamma_\pm = \log (m_{Ag^+}/m^0_{Ag^+}) \qquad (1)$$

Values of m_{Ag^+} were inferred from the e.m.f. using the empirical calibration formula

$$\text{e.m.f.} = 0.55074 + 0.05910 \log m_{Ag^+} - 0.01254\sqrt{\mu}$$

where μ is the ionic strength.

Since $m^0_{Ag^+}$ was not determined, only relative values of $\gamma_\pm$ (relative to $\gamma_\pm$ at 0.05 m $NaNO_3$) are reported in Table I.

TABLE I

RELATIVE ACTIVITY COEFFICIENTS OF SILVER SUCCINATE AND SEBACATE

	Silver succinate		Silver sebacate	
$\sqrt{\mu}$	E.m.f. (v.)	$-\log \gamma_\pm/\gamma_\pm^{(0.05)}$	E.m.f. (v.)	$-\log \gamma_\pm/\gamma_\pm^{(0.05)}$
0.224	0.35440	0.000	0.32850	0.000
.316	.35905	.099	.33310	.098
.447	.36320	.196	.33520	.161
.548	.36387	.229	.33638	.202
.707	.36612	.301	.33670	.241
.837	.36685	.341	.33615	.259
1.000	.36780	.391	.33625	.296
1.225	.36732	.431	.33473	.318
1.414	.36638	.455	.33430	.351
1.581	.36647	.492	.33360	.374

The ionic strength in Table I is actually only the sodium nitrate contribution. The additional contribution due to the silver salts was estimated in the following way to be small. In a dilute solution of 0.05 m $NaNO_3$ the value of $\gamma_\pm$ for a 2–1 electrolyte can be found approximately from the Guntelberg expression[6] to be 0.65. Introducing this and the corresponding m_{Ag^+} into eq. 1, $m^0_{Ag^+}$ is estimated to be about $3.4 \cdot 10^{-4}$ and $1.3 \cdot 10^{-4}$ m for silver succinate and sebacate, respectively. The corresponding contributions to $\sqrt{\mu}$ when μ is 0.05 m are only 1 and 0.5% and may be ignored for the present purposes.

The use of the calibrated potentiometric method for measurement of the silver ion concentration tacitly assumed that electrochemically the dilute silver dicarboxylate and nitrate in aqueous sodium nitrate behave similarly. This assumption is valid when the silver salt makes only a small contribution to $\sqrt{\mu}$, a condition which was just seen to be adequately satisfied for the data of Table I. A few calibration points obtained at $\sqrt{\mu}$'s less than 0.2 showed appreciable deviation from the calibration equation. For the reasons cited a different type of measurement will be necessary to determine the solubility of the silver salts at low μ's and the absolute value of the $\gamma_\pm$'s in Table I.

To test the possibility of experimentally significant ion pair formation between silver ions and the dicarboxylate anions, a small amount of a sodium dicarboxylate (to make 10^{-5} M) was added to a solution of 2×10^{-5} M $AgNO_3$ in a solution containing excess sodium nitrate. No detectable e.m.f. change (0.1 mv. detection limit) was found indicating negligible change in activity coefficient of the silver salt (*i.e.*, less than 1%).

Discussion

Two of the major factors influencing activity coefficients are electrostatic and hydration effects.[6b] The latter becomes increasingly important with increasing electrolyte concentration: the ions bind some solvent so that the solution is effectively more concentrated than the molality itself implies. In the present system the silver salts are so dilute that they will bind only a negligible fraction of the solvent. The extent of bound solvent will therefore be the same in silver succinate and sebacate solutions containing a given sodium nitrate concentration. Accordingly, the difference in chemical potential of the two silver salts in these two solutions will be independent of this hydration effect.[7] The same remarks apply to the ratio of mean ion activity coefficients of these salts. Relative values of this ratio are computed from the data of Table I and are plotted in Fig. 1, together with a theoretical curve which will now be discussed.

Because of their dilution the ions of the silver salts will interact primarily with those of sodium nitrate rather than with themselves. Accordingly the chemical potential of the silver ions will be the same in both solutions and attention can be focused on that of the dicarboxylate ions. Denoting by γ the single ion activity coefficient of a dicarboxylate ion, by γ^{el} its electrostatic factor, and by the subscripts A and B the succinate and sebacate, respectively, eq. 2 obtains in the present system.

$$\log \gamma_{\pm,A}/\gamma_{\pm,B} = \frac{1}{3} \log \gamma_A/\gamma_B = \frac{1}{3} \log \gamma_A^{el}/\gamma_B^{el} \qquad (2)$$

(5) I. Iwasaki, *Bull. Chem. Soc. Japan*, **25**, 226 (1952).

(6) (a) E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); (b) *cf.* R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955.

(7) This tacitly assumes a model in which the number of bound solvent molecules is the same for all important ionic configurations occurring at a given ionic concentration. This model is the one generally employed.

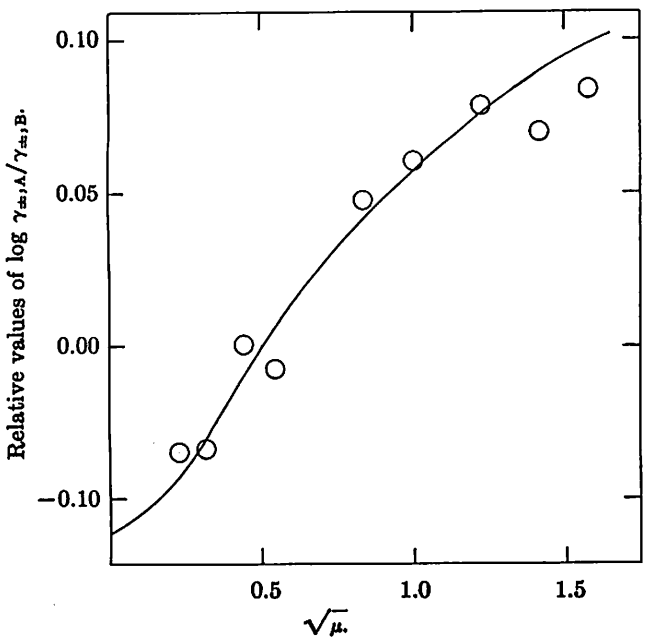

Fig. 1.—Ionic strength dependence of the ratio of mean ion activity coefficients of silver sebacate ($\gamma_{\pm,B}$) and succinate ($\gamma_{\pm,A}$). The value of log $\gamma_{\pm,B}/\gamma_{\pm,A}$ relative to its value at $\sqrt{\mu}$ = 0.5 is plotted: experimental, O; theoretical, —.

For simplicity, the model to be used for the computation of γ^{el} will be the same as that employed by Bjerrum[8] for his treatment of the successive ionization constants of dicarboxylic acids. He treated the two ionized groups of the dicarboxylate ion as two point charges separated by a distance r in the solvent and he related the ratio of the ionization constants to the Coulombic repulsion. From his expression, the values of r estimated for succinate[9] and for sebacate[10] ions are 3.65 and 13 A., respectively. Considering the approximation, these r's are moderately close to the actual values. However, for very short chain length dicarboxylic acids this equation is less valid and a more elaborate model[11] is needed.

In the approximation to be employed here molal and rational aetivity coefficients may be taken to be the same. The two charges 1 and 2 will be denoted by Z_1e and Z_2e, respectively. A charging process will be considered such that at any stage each charge of the bipolar ion has a fraction λ of its final value, Z_ie. The distances of the field point from these two point charges will be denoted by r_1 and r_2. It may then be shown by standard methods that at any stage of the charging process the solution of the linearized Poisson–Boltzmann equation for the electrostatic potential ψ satisfying the boundary conditions of the model ($\psi \to 0$ as r_1 and $r_2 \to \infty$; $\psi \to \lambda Z_ie/Dr_i$ + constant as $r_i \to 0$, where i = 1,2) is given by

$$\psi(r_1, r_2) = \frac{\lambda Z_1 e}{Dr_1} e^{-\kappa r_1} + \frac{\lambda Z_2 e}{Dr_2} e^{-\kappa r_2}$$

where κ^2 has its usual value,[5b] $8\pi e^2\mu/DkT$.

Subtracting from this expression the self-potential of ion i (i = 1,2) the remaining contribution to ψ at r_i = 0 will be designated by ψ_i^0. The work required to charge up the bipolar ion at a given ionic strength is

$$\sum_{i=1}^{2} \int_{\lambda=0}^{1} \psi_i^0 d(\lambda Z_i e)$$

Subtracting from this the work required to charge up this ion when K = 0, the electrostatic contribution to the chemical potential of the bipolar ion is found to be

$$kT \ln \gamma^{el} = -\frac{(Z_1^2 + Z_2^2)e^2\kappa}{2D} + \frac{Z_1Z_2e^2\kappa}{D} \frac{e^{-\kappa r} - 1}{\kappa r} \quad (3)$$

Alternatively, when $Z_1 = \pm Z_2$ this equation may be deduced as a special case of a more elaborate model due to Scatchard and Kirkwood.[12] These authors treated the two charges as spheres of radii a separated by a fixed distance r. They solved the differential equation for ψ inside and outside the spheres in an approximate way which becomes increasingly exact as a approaches zero. Their equation becomes identical with eq. 3 when a is set equal to zero there and Z_1 is set equal to $\pm Z_2$ in eq. 3.

Equation 3 may also be compared with that obtained[13] for an ellipsoidal model of a dipolar ion in solutions of very low ionic strength. The two charges were assumed to lie at the foci of the ellipsoid. When the eccentricity of the ellipsoid approaches unity, the latter degenerates into a straight line and the model becomes in fact one of two point charges. The resulting equation should therefore be identical with eq. 3 when one sets $Z_1 = Z_2 = -1$ there and expands eq. 3 in a power series in κr, retaining only the first term

$$kT \ln \gamma^{el} = -e^2\kappa^2 r/2D \quad (4)$$

This is indeed the case.[14]

Equation 3 approaches the simple Debye–Hückel expression for a single localized charge $(Z_1 + Z_2)e$ when the ionic atmosphere is sufficiently far removed. This occurs when Kr is small. It approaches that for two isolated localized charges (plus a now-shielded Coulombic repulsion term $Z_1 Z_2 e^2/Dr$) when the atmosphere is drawn in close about each charge (large κr). The transition region occurs at $\kappa r \sim 1$ when $Z_1 \sim Z_2$.

Introducing into eq. 3 the r-values obtained earlier for sebacate and succinate ions, the curve of Fig. 1 was computed. The agreement with the data is surprisingly close. From eq. 3 it may be inferred that the transition discussed in the preceding paragraph occurs at low ionic strengths for sebacate ion and an ionic strength of the order of 0.7 m for the succinate ion ($\kappa \sim 1/r$ where r = 3.65 Å.).

Similar remarks concerning a transition region apply to activated complexes of chemical reactions consisting of two separated charge centers. When

(8) N. Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

(9) This estimate is based on the ionisation constants of G. D. Pinching and R. G. Bates, *J. Research Natl. Bur. Standards*, **45**, 322 (1050).

(10) *Cf.* F. H. Westheimer and M. W. Shookhoff, *J. Am. Chem. Soc.*, **61**, 555 (1939). These authors summarize the r-values obtained by application of the simple Bjerrum expression to all dicarboxylate ions up to sebacate. The r-value for sebacate can then be obtained by a straightforward extrapolation.

(11) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

(12) G. Scatchard and J. G. Kirkwood, *Phys. Z.*, **33**, 297 (1932).

(13) J. G. Kirkwood in "Proteins, Amino Acids and Peptides," edited by E. J. Cohn and J. J. Edsall, Reinhold Publ. Corp., New York, N. Y., 1939, Chap. 12.

(14) A typographical error of a factor of two in eq. 17 of ref. 12 disappears in eq. 18 there.

Z_1 and Z_2 are about equal the usual assumption that this complex behaves as a single charge in its interaction with its atmosphere is a reasonable one according to eq. 3 if $\kappa << r^{-1}$. In the case of many isotopic exchange reactions it is expected that r is of the order of 7 Å. and therefore that this behavior would be exhibited at μ's appreciably below $0.2m$. Because of the highly specific interactions which occur between multiply charged ions of opposite sign these remarks apply primarily to an "inert" salt medium consisting of a 1–1 electrolyte.

The linear dependence of the activity coefficient of a zwitterion on the ionic strength in dilute solution, embodied in eq. 4, has been abundantly confirmed experimentally. We have found that application of eq. 4 to the experimental data of Cohn and others[15] yields r-values for amino acids which are in fair agreement with those inferred from pH data using the simple Bjerrum (Coulombic) expression. When the amino acids are small these r's are somewhat less than those estimated on the basis of free rotation about the bonds in these molecules.

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(15) *Cf.* Reference 12 and Chap. 11 in that monograph.