Activity Coefficients in Aqueous Carboxylic Acid–Sodium Carboxylate Solutions

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The distribution of formic, acetic, and propionic acids between water and butyl ether and between sodium carboxylate solutions and butyl ether was studied over a wide range of acid and salt concentrations. The data for the water–butyl ether systems were correlated using a model which assumes the existence of an acid dimer in the organic phase. The distribution and dimerization constants were used in conjunction with the distribution data involving the salt solutions to calculate molar and molal activity coefficients for the carboxylic acids in the carboxylate solutions. Molal activity coefficients of the sodium carboxylates were obtained using the cross-differentiation relationship.

ALTHOUGH ACTIVITY COEFFICIENTS have been obtained for the C_1 to C_4 carboxylic acids in aqueous solution (*6*) and for the aqueous C_1 to C_9 sodium carboxylates (*10*), only a few results are available for aqueous mixtures of carboxylic acids and their corresponding carboxylate salts (*2, 8*). The present study provides activity coefficients at 25° C. for the C_1 to C_3 carboxylic acids and sodium carboxylates in their mixtures in the 0 to 1*M* acid and 0 to 4*M* salt concentration range.

EXPERIMENTAL

Fisher reagent grade formic, acetic, and propionic acids and the corresponding sodium salts were used without further purification. Analysis of the dried salts by perchloric acid titration in glacial acetic acid indicated that they contained between 97 and 98% titratable carboxylate. The exact values from these titrations were utilized in establishing salt concentrations in the aqueous phases of the distribution mixtures. Eastman practical grade dibutyl ether was freed from peroxides by the method of Feinstein (*3*) with additional passage through activated alumina to remove polar impurities.

Distribution Measurements. Distributions were carried out in 250-ml. bottles (Scientific Glass Apparatus Co.) fitted with O-ring ground-glass stoppers. Solutions of the acid-salt mixture under study were equilibrated with dibutyl ether for several days in a water bath maintained at 25.0° C. ± 0.07°. In preparing the distribution mixtures, precautions were taken to minimize both salt concentration changes in the aqueous phase and peroxide formation. Separate experiments were done to determine the time necessary to reach equilibrium and the solubility of the carboxylate salts in butyl ether. This solubility was found to be negligible.

Analysis of Distribution Mixtures. The separated phases were analyzed by electrometric titration of the acid, using standard solutions of carbonate-free NaOH as the titrant. A Beckman Zeromatic pH meter was used in conjunction with a Leeds & Northrup Model H AZAR recorder for added sensitivity in the determination of the end point. Beckman No. 41262 general purpose glass electrodes and Radiometer K100 calomel electrodes were used to monitor the titrations. Titrations were always carried out in duplicate. All glassware and burets used in these determinations were calibrated. Appropriate corrections were also made for the variations in volumes of the aliquots taken, produced by changes in ambient temperature.

The presence of dibutyl ether led to difficulties in the titration of the carboxylic acid in the organic phase. This problem was circumvented by quantitatively extracting the acid sample back into water before analysis as follows. An aliquot of the acid in ether was placed in a test tube. The acid was then extracted into water by successive introduction, shaking, and removal of small portions of water. Calibration with ether solutions of known acid concentration established the number of repetitions of this procedure necessary for quantitative extraction.

RESULTS

Distribution Equilibria of Carboxylic Acids. Data were obtained initially for the distribution of the acids between water and dibutyl ether. These results are shown in Table I, where C_T^o and C_T^w stand for the concentration of acid in moles per liter obtained by titration of the organic (*o*) and water (*w*) phases, respectively. These data are the average of duplicate titrations which usually deviated from each other by less than 0.2% and never more than 0.5%. The column headed C_T^w (1–β) gives the concentration of undissociated acid, C_{HA}^w, in the aqueous phase. The fraction of acid ionized, β, was calculated from data given by Harned and Owen (*4*). Finally, the distribution coefficient is calculated as C_T^o/C_T^w (1–β).

The rise in the distribution coefficient with increasing acid concentration has been found in a wide variety of similar systems. The generally accepted interpretation is that of dimerization of the acids in the organic phase. It is useful to apply this model to the data, since the correlations obtained are an aid in further calculation.

The equilibria considered and the associated equilibrium constant expressions are as follows:

$$HA\,(\text{aq}) \rightleftharpoons HA\,(\text{org});\quad K_d = \frac{C_{HA}^o}{C_{HA}^w} \cdot \frac{1}{y_{HA}^w} \tag{1}$$

$$2HA\,(\text{org}) \rightleftharpoons H_2A_2(\text{org});\quad K_2^o = \frac{C_{H_2A_2}^o}{(C_{HA}^o)^2} \tag{2}$$

The symbols C_{HA}^o and $C_{H_2A_2}^o$ are the concentrations of the monomeric acid and acid dimer in the organic phase. The molar activity coefficient of the monomeric acid in pure water is denoted by y_{HA}^w. The assumption is implicit in Equations 1 and 2 that the solute in the organic phase forms an ideal associated solution with the activity

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Table I. Distribution of Carboxylic Acids between Water and Dibutyl Ether

C_T^o	C_T^w	$C_T^w(1-\beta)$	Distribution Coefficient
	Formic Acid		
0.01215	0.2492	0.2418	0.05025
0.02061	0.4186	0.4101	0.05026
0.02732	0.5485	0.5386	0.05072
0.03732	0.7494	0.7380	0.05057
0.04640	0.9318	0.9191	0.05048
0.05750	1.143	1.129	0.05093
	Acetic Acid		
0.003222	0.04502	0.04414	0.07300
0.007114	0.09852	0.09721	0.07295
0.007528	0.1046	0.1032	0.07318
0.01406	0.1906	0.1888	0.07447
0.01990	0.2689	0.2667	0.07462
0.02173	0.2922	0.2899	0.07496
0.03435	0.4524	0.4496	0.07640
0.04166	0.5418	0.5387	0.07733
0.05010	0.6385	0.6351	0.07889
0.05506	0.6950	0.6915	0.07922
0.06569	0.8165	0.8127	0.08083
	Propionic Acid		
0.02622	0.07268	0.07169	0.3657
0.05360	0.1410	0.1396	0.3840
0.08943	0.2226	0.2209	0.4048
0.1748	0.3948	0.3925	0.4454
0.2133	0.4630	0.4605	0.4632
0.3061	0.6173	0.6144	0.4982
0.3946	0.7442	0.7410	0.5325
0.4972	0.8937	0.8903	0.5585

Table II. Parameters Characterizing Distribution of Carboxylic Acids between Water and Dibutyl Ether

Acid	K_d	K_2^o, Liters/Mole
Formic	0.05012 ± 0.00018	0.124 ± 0.054
Acetic	0.07199 ± 0.00014	1.016 ± 0.041
Propionic	0.3458 ± 0.0014	1.184 ± 0.023

The reported uncertainties for K_d and K_2^o are standard deviations.

Table III. Distribution of Formic Acid between Aqueous Sodium Formate Solutions and Dibutyl Ether

C_T^o	C_T^{ws}	$\log y_{HA}^{ws}$	C_T^o	C_T^{ws}	$\log y_{HA}^{ws}$
1.000*M* Sodium Formate			2.000*M* Sodium Formate		
0.01672	0.3798	−0.0581	0.01202	0.3014	−0.1014
0.02607	0.5860	−0.0546	0.01492	0.3742	−0.1007
0.03394	0.7676	−0.0581	0.01929	0.4947	−0.1116
0.03990	0.9063	−0.0607	0.02742	0.7036	−0.1123
0.05124	1.166	−0.0622	0.03472	0.8882	−0.1119
			0.04631	1.179	−0.1109
3.000*M* Sodium Formate			4.000*M* Sodium Formate		
0.01754	0.4969	−0.1547	0.01237	0.3824	−0.1914
0.02094	0.5965	−0.1569	0.01406	0.4314	−0.1884
0.02634	0.7515	−0.1587	0.01907	0.6042	−0.2038
0.03100	0.8887	−0.1611	0.02478	0.7968	−0.2122
0.03818	1.101	−0.1641	0.02642	0.8471	−0.2159
			0.02904	1.040	−0.2098
			0.03631	1.191	−0.2214

Table IV. Distribution of Acetic Acid between Aqueous Sodium Acetate Solutions and Dibutyl Ether

0.500*M* Sodium Acetate

C_T^o	C_T^{ws}	$\log y_{HA}^{ws}$
0.01649	0.2184	0.0069
0.05946	0.7378	0.0039
0.09112	1.084	0.0030

1.000*M* Sodium Acetate

C_T^o	C_T^{ws}	$\log y_{HA}^{ws}$
0.01432	0.1934	0.0004
0.01502	0.2003	0.0048
0.03769	0.4850	0.0030
0.06216	0.7594	0.0090
0.09000	1.075	0.0020

2.919*M* Sodium Acetate

C_T^o	C_T^{ws}	$\log y_{HA}^{ws}$
0.008392	0.1146	−0.0004
0.01286	0.1796	−0.0137
0.02512	0.3422	−0.0120
0.03378	0.4544	−0.0133
0.04122	0.5558	−0.0195
0.06046	0.8009	−0.0249
0.06954	0.9130	−0.0269
0.08430	1.090	−0.0294

2.000*M* Sodium Acetate

C_T^o	C_T^{ws}	$\log y_{HA}^{ws}$
0.01418	0.1897	0.0048
0.01473	0.1962	0.0056
0.01538	0.2035	0.0082
0.03329	0.4325	0.0026
0.04739	0.6102	−0.0039
0.05746	0.7232	−0.0009
0.06332	0.7976	−0.0048
0.07638	0.9498	−0.0073
0.08016	0.9906	−0.0069
0.09480	1.152	−0.0082
0.09666	1.182	−0.0124

3.892*M* Sodium Acetate

C_T^o	C_T^{ws}	$\log y_{HA}^{ws}$
0.008622	0.1271	−0.0338
0.01888	0.2780	−0.0402
0.01898	0.2780	−0.0390
0.02706	0.3992	−0.0480
0.02718	0.4012	−0.0480
0.03266	0.4807	−0.0515
0.03298	0.4856	−0.0519
0.04055	0.5934	−0.0546
0.04906	0.7166	−0.0599
0.07510	1.098	−0.0770

coefficients of the monomer and dimer equal to unity.

An equation for the calculation of K_d and K_2^o may be derived (*1*) by combining Equations 1 and 2 with the mass balance condition, $C_T^o = C_{HA}^o + 2C_{H_2A_2}^o$. The equation is

$$\frac{C_T^o}{C_T^w(1-\beta)y_{HA}^w} = K_d + 2K_2^oK_d^2y_{HA}^w[C_T^w(1-\beta)] \qquad (3)$$

The activity coefficients, y_{HA}^w, for the carboxylic acids in water which are necessary for the evaluation of K_d and K_2^o by the use of this equation were calculated from the cryoscopic data of Jones and Bury (*6*) with the appropriate thermal data being obtained or estimated from both the International Critical Tables (*5*) and the National Bureau of Standards (*9*). Corrections were made for the ionization of the acids using the data of Harned and Owen (*4*). These calculations indicate that the molar activity coefficients for aqueous formic and acetic acids are within 0.5% of unity over the concentration range of interest. On the other hand, the molar activity coefficient of propionic acid decreases to 0.954 at $C_{HA}^w = 0.8903M$. Since Equation 3 is a linear form if the left side is taken as the dependent variable and $C_T^w(1-\beta)$ as the independent variable, a least-squares treatment could be employed to obtain K_d and K_2^o for each acid, using the calculated activity coefficients and the data of Table I. The results are given in Table II.

Salt Effects on Distribution Equilibria. The results of the experiments involving the partition of the carboxylic acids between dibutyl ether and the sodium carboxylate solution are given in Tables III through V, where C_T^o and C_T^{ws} are the molar concentrations of acid determined by titration of the organic (*o*) and aqueous sodium carboxylate (*ws*) phases, respectively. The presence of relatively large concentrations of sodium carboxylate in the aqueous phase makes a correction of C_T^{ws} for ionization of the acids unnecessary—i.e., $C_T^{ws} = C_{HA}^{ws}$. The columns of the tables headed log y_{HA}^{ws} give the logarithm of the activity coefficient of the carboxylic acid in the salt solution. This quantity is calculated in the following manner (*7*).

We consider two distribution experiments. In one, the carboxylic acid partitions between water and the organic phase. In the other, the acid distributes between the carboxylate salt solution and the organic phase. If the concentration of acid in the organic phase at equilibrium is the same in the two experiments, then

$$a_{HA}^w = a_{HA}^{ws} \qquad (4)$$

Table V. Distribution of Propionic Acid between Aqueous Sodium Propionate Solutions and Dibutyl Ether

C^o_T	C^{ws}_T	$\log y^{ws}_{HA}$	C^o_T	C^{ws}_T	$\log y^{ws}_{HA}$
0.500*M* Sodium Propionate			1.000*M* Sodium Propionate		
0.08728	0.2011	0.0286	0.03757	0.09004	0.0472
0.1400	0.3176	0.0111	0.1247	0.2648	0.0414
0.2634	0.5108	0.0170	0.2288	0.4398	0.0346
0.3964	0.7052	0.0094	0.2955	0.5402	0.0306
0.5256	0.8727	0.0060	0.5806	0.9162	0.0140
2.000*M* Sodium Propionate			3.000*M* Sodium Propionate		
0.05007	0.1156	0.0535	0.03648	0.09050	0.0334
0.1652	0.3314	0.0444	0.1111	0.2688	−0.0077
0.2892	0.5339	0.0286	0.1326	0.2985	0.0115
0.4085	0.7155	0.0128	0.2342	0.5142	−0.0252
0.6091	0.9922	−0.0062	0.3554	0.7651	−0.0607
4.000*M* Sodium Propionate			0.4513	0.9642	−0.0856
0.04106	0.1322	−0.0838			
0.1146	0.3548	−0.1179			
0.2006	0.6246	−0.1628			
0.2891	0.9346	−0.2148			
0.3044	1.023	−0.2370			

where a^w_{HA} and a^{ws}_{HA} are the activities of the carboxylic acid in the various phases indicated by the previously defined superscripts. There is the implicit assumption in Equation 4 that the variation in water activity in the organic phase produced by the addition of salt to the aqueous phase does not influence the activity coefficient of the acid in the organic phase. Support for this assumption is provided by Sykes and Robertson (*11*). They obtained activity coefficients for the isomeric nitrobenzoic acids in NaCl and $MgSO_4$ solutions over a wide salt concentration range by both solubility and distribution measurements. The results obtained by the different methods were in good agreement. Since the reference phase was pure solid in the solubility studies, while it was water-saturated organic solvent in the distribution experiments, variable water activity appeared to have no effect on the results obtained.

Equation 4 may be solved for the activity coefficient, y^{ws}_{HA}, since $a^{ws}_{HA} = y^{ws}_{HA}C^{ws}_{HA}$ and therefore

$$y^{ws}_{HA} = \frac{a^w_{HA}}{C^{ws}_{HA}} \tag{5}$$

In each case, the value of a^w_{HA} was calculated by rearranging Equation 3 to yield

$$a^w_{HA} = \frac{-1 + (1 + 8K^o_2C^o_T)^{1/2}}{4K_dK^o_2} \tag{6}$$

and substituting into this equation the value of C^o_T which was found at equilibrium in the distribution experiment involving the salt solution.

Correlation of Results. Equations for the dependence of the molar activity coefficients of the carboxylic acids given in Tables III to V on acid and salt concentration were obtained using an IBM 360-40 computer. Both a conventional least-squares procedure and a more general minimization routine (Simplx, J. P. Chandler, University of Indiana) were used with equivalent results. An empirical equation of the form

$$\log y^{ws}_{HA} = AC_s + BC^2_s + CC^3_s + DC^{ws}_{HA} + EC_sC^{ws}_{HA} \tag{7}$$

where C_s and C^{ws}_{HA} are the concentrations of sodium carboxylate and carboxylic acid, respectively, was found to be the simplest polynomial that would give an acceptable fit to the data for propionic acid–sodium propionate mixtures.

Table VI. Parameters for Representation of Log y^{ws}_{HA} by Equation 7

Acid	$A \times 10^2$	$B \times 10^3$	$C \times 10^3$	$D \times 10^3$	$E \times 10^2$	$\sigma \times 10^3$
Formic	−5.21	1.66	. . .	−1.55	−0.754	4.05
Acetic	1.88	−6.90	. . .	1.73	−1.01	3.31
Propionic	6.29	−7.74	−2.95	−2.96	−4.18	5.57

Table VII. Parameters for Representation of Log γ^{ws}_{HA} by Equation 8

Acid	$A' \times 10^2$	$B' \times 10^3$	$C' \times 10^3$	$D' \times 10^2$	$E' \times 10^3$	$\sigma \times 10^3$
Formic	−6.34	2.47	. . .	−1.72	−3.87	4.05
Acetic	−0.731	−3.55	. . .	−2.08	−5.06	2.78
Propionic	4.63	−20.7	1.04	−5.56	−10.6	6.15

The results for the other acid-salt mixtures could be expressed without the use of the term in C^3_s. Table VI gives the parameters to be used in Equation 7 for each acid-salt mixture. The last column in Table VI gives the standard deviation of the fit, $\sigma = \{\delta^2/(n-k)\}^{1/2}$, where δ is the difference between the observed and calculated values of log *y*, *n* is the number of points in the set of data, and *k* is the number of coefficients used in Equation 7 for a particular acid-salt mixture.

The activity coefficient of the sodium carboxylates in these solutions may be obtained from the above results by the use of the cross-differentiation relationship (see below). In doing this calculation, it is convenient to have the activity coefficients on the molal scale. The data in Tables III to V were therefore recalculated in terms of molalities. The densities of the carboxylic acid–sodium carboxylate solutions which were necessary for this calculation were estimated from the densities of the single component solutions given in the International Critical Tables (*5*). The resulting calculated molal activity coefficients of the carboxylic acids γ^{ws}_{HA} could be expressed in terms of acid and salt molalities, m^{ws}_{HA} and m_s, respectively, by means of the equation

$$\log \gamma^{ws}_{HA} = A'm_s + B'm^2_s + C'm^3_s + D'm^{ws}_{HA} + E'm_sm^{ws}_{HA} \tag{8}$$

Here again, the term in m^3_s is needed only for the propionic acid–sodium propionate solution. Table VII gives the values of the parameters and the standard deviations obtained by a least-squares fit of the molal activity coefficients. These parameters apply to the concentration ranges, 0 to 1.5 molal salt and 0 to 5 molal acid.

Application of the cross-differentiation relationship

$$2\left(\frac{\partial \ln \gamma_s}{\partial m^{ws}_{HA}}\right)_{m_s} = \left(\frac{\partial \ln \gamma^{ws}_{HA}}{\partial m_s}\right)_{m^{ws}_{HA}} \tag{9}$$

to Equation 8 and integration with respect to m^{ws}_{HA} at constant m_s yield an expression for the dependence of the molal activity coefficient of the sodium carboxylates in these solutions on salt and acid concentration. The equation is

$$\log \gamma_s = \log \gamma^o_s + \tfrac{1}{2}A'm^{ws}_{HA} + B'm_sm^{ws}_{HA} + \tfrac{3}{2}C'm^2_sm^{ws}_{HA} + \tfrac{1}{4}E'(m^{ws}_{HA})^2 \tag{10}$$

where log γ^o_s is the molal activity coefficient of the salt in a solution containing no acid. The values of the parameters for use in Equation 10 may be found in Table VII.

ACKNOWLEDGMENT

We are grateful to R. A. Robinson for his advice and assistance.

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RECEIVED for review November 6, 1967. Accepted October 14, 1968. Investigation supported in part by Public Health Service Research Grant GM-11762 from the Institute of General Medical Sciences. Based on the thesis submitted by J. L. Czeisler to the Graduate School of State University of New York at Binghamton in partial fulfillment of the requirements for the M.A. degree, June 1966.

Solvent Vapor Pressures over Dilute Solutions of Tin in Mercury

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The isopiestic balance has been used to measure mercury vapor pressures over dilute solutions of tin in mercury at 523° K. These measurements were made on alloys varying in composition from 0.90774 to 0.99847 mole fraction of mercury. These results do not seem to be described by a simple mathematical function and do not approach ideal behavior in the region of measurement. Deviations from a smooth curve through the data are not greater than 0.0003 in the activity (0.3 gram cal. in the mercury partial molar free energy), and the agreement with other work is excellent.

THE ISOPIESTIC BALANCE has been used to make highly precise measurements of the cadmium vapor pressure over cadmium solutions containing small amounts of solute (*3, 4, 11*). Cadmium vapor pressures have been measured with apparent high accuracy at compositions as great as 0.9984 mole fraction. The present work extends the use of this balance to measurement of mercury vapor pressures over dilute solutions with tin as the minor component.

EXPERIMENTAL

Equipment. The general construction of the balance has been described (*2, 4*). Briefly, the isopiestic balance consists of a quartz tube contained in a furnace and suspended by a balance system. The tube consists of two vertical legs joined at their tops by a horizontal section. One leg contains the alloy, the other pure mercury condensate. The furnace surrounding the quartz tube contains four separate heaters which independently control the temperatures of each leg and of each half of the horizontal section. The top is maintained at a higher temperature than either leg, to prevent condensation. The quartz tube is mounted on a frame suspended from two fine wires and is counterbalanced so that it may pivot freely.

A side arm of the frame is attached by a third fine wire to an analytical balance. As mercury transfers from the alloy reservoir to the mercury reservoir the weights on the analytical balance must be adjusted to return the balance to its null position. The dimensions of the isopiestic balance system cause a weight shift at the analytical balance to be six times greater than the weight of mercury transferred. When no weight shift is occurring at the analytical balance, the mercury vapor pressure over the alloy and over the pure mercury condensate is the same. The alloy must necessarily be at a higher temperature than the mercury when no weight transfer is taking place. This temperature difference is measured directly with a Pt-Pt-10% Rh thermocouple pair, each junction being placed about 0.5 inch from the bottom of one of the two quartz legs. To assure nearly identical compositions the hot and cold junctions are made by cutting both types of wire and forming the two junctions at the cuts. The absolute temperature of the alloy reservoir is also measured. Copper wire is used to connect the various thermocouples to the potentiometer through a switch. All junctions between the thermocouples and the copper wire are placed side by side in an ice bath, with direct contact prevented by their individual containment in thin sleeves of plastic tubing. The relative positions of these junctions to each other are permanently fixed to eliminate spurious effects. On one of the balances these junctions are further contained in an aluminum block.

From a knowledge of mercury vapor pressure variation with temperature, the vapor pressure of the mercury over the alloy can be calculated. The composition of the alloy can be changed as desired, by condensation into or evaporation from the pure mercury reservoir. The composition of the alloy for any given measurement can be determined from the corresponding analytical balance reading.

Procedure. The original surfaces of reagent grade tin (99.9% purity by manufacturer's analysis) were removed by cutting. Then the tin was washed, first with reagent grade acetone, then with analytical reagent petroleum ether. Triple-distilled mercury was further purified by slow distillation from a tube containing uranium to remove oxide.

The isopiestic balance equilibration tube with a secondary U-tube attached was evacuated to 10^{-8} atm., flamed, then filled with argon. Tin was placed in one leg of the balance tube, mercury was loaded into the secondary tube, then the system was again evacuated to 10^{-8} atm. and flamed. The secondary tube was sealed off from the vacuum system, and part of the mercury was evaporated from the secondary tube into the horizontal section of the balance tube. Finally the balance tube was sealed off, separated from the secondary tube, and attached to the frame in the isopiestic balance. Slow distillation from the horizontal section into