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The Relation between Equilibrium Constants in Water and in Other Solvents

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The equilibrium constants, in two different solvents, of a reaction

$$aA + bB + \cdots \rightleftarrows dD + eE + \cdots \qquad (1)$$

are related to the distribution coefficients of the various components between the phases by the equation

$$K''/K' = D_A^a D_B^b \cdots / D_D^d D_E^e \cdots \qquad (2)$$

In this equation, which was first derived by Nernst,[1] K' and K'' are the equilibrium constants in the first and second solvents, respectively, and D is the distribution coefficient between the two phases of a given reaction component.[2]

The distribution coefficient of a given component is defined as the ratio of the activities of the component in the two phases at distribution equilibrium. For example, the distribution coefficient of component A is defined by

$$D_A = (a'_A/a''_A)_{\text{equil.}} \qquad (3)$$

in which the superscipts (′) and (″) refer to the first and second phases, respectively.

If reaction (1) involves only *uncharged* substances the various distribution coefficients can be determined accurately by classical methods, and hence an experimental test of eq. (2) can be made easily. However, if the reaction involves *ionic* components, such an experimental test is much more difficult, because it is impossible to determine unambiguously the *absolute* value of the distribution coefficient of a single species of ion.

The transfer of a single ionic species between two phases would involve a certain amount of electrical work in addition to purely mechanical work (difference in chemical potential between the two phases). The amount of electrical work will depend on the difference in the electrical potentials of the two phases (phase boundary potential), and since this potential difference cannot be determined in an exact way, the absolute value of the distribution coefficient of a single ionic species never can be evaluated unambiguously. Detailed discussions of this subject have been given by Guggenheim,[3] Brönsted[4] and Donnan and Guggenheim.[5]

In an ingenious study of the ionization constants of various acids in water and ethanol, Bjerrum and Larsson[6] attempted to determine the distribution coefficients of individual ionic species by measuring the e. m. f. of cells comprised of an indicator electrode for the ion in question in water and in ethanol. They tried to eliminate the potential at the junction of the two solvents by the use of concentrated salt bridges. Values obtained in this way are approximate only, because it is impossible to eliminate completely the liquid junction potential.

Fortunately, a knowledge of the absolute values of individual ionic distribution coefficients is not essential, because it is possible to determine the products and quotients of individual ionic distribution coefficients in an exact way and these suffice for the purpose.

From the solubilities s_1 and s_2 of a uni-univalent salt AB in two solvents we find

$$D_A D_B = \left(\frac{s_1}{s_2}\right)^2 \frac{\gamma'_A \gamma'_B}{\gamma'_A \gamma''_B} \qquad (4)$$

in which γ denotes the activity coefficient.

From the values of the standard electrode potentials of an ion i in two solvents, the ratio of the distribution coefficient of that ion to the distribution coefficient of the hydrogen ion between the two solvents is given by the relation

$$E^{0\prime} - E^{0\prime\prime} = \frac{RT}{F} \ln \frac{D_H}{D_i} \qquad (5)$$

in which $E^{0\prime}$ and $E^{0\prime\prime}$ represent the standard electrode potentials of the ion i in solvents 1 and 2, respectively.

In the present study the ionization constants of several weak acids in water, methanol and ethanol are compared. If pK represents the negative logarithm of the ionization constant, it can be shown from equation (2) that

$$pK'' - pK' = \Delta pK = \log D_H D_A - \log D_{HA} \qquad (6)$$

The single primes refer to water, and the double primes to alcohol, while the subscripts H, A and

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[1] W. Nernst, *Z. physik. Chem.*, **9**, 137 (1892); **13**, 531 (1894); *Ann. Physik*, [4] **8**, 600 (1902).

[2] A. E. Hill, in Taylor's "Treatise of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1936, p. 483.

[3] E. A. Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929); **34**, 1540 (1930).

[4] J. N. Brönsted, *Z. physik. Chem.*, **143**, 301 (1929).

[5] F. G. Donnan and E. A. Guggenheim, *ibid.*, **A162**, 346 (1932).

[6] N. Bjerrum and E. Larsson, *ibid.*, **127**, 368 (1927).

HA refer to hydrogen ion, the anion of the weak acid and undissociated part of the acid, respectively. The product D_HD_A was found as follows. The solubility of the silver salt of the acid was determined in water and in the two alcohols. These data gave $D_{Ag}D_A$ for water–ethanol and water–methanol, using equation (4). By means of the values of the standard electrode potentials of the silver ion in water, methanol and ethanol[7] the value of the ratio D_H/D_{Ag} was calculated by equation (5). The product of $D_{Ag}D_A$ by D_H/D_{Ag} is D_HD_A. The value of D_{HA} was calculated from the solubility ratios of the uncharged acid, allowing for the ionized part if necessary, and assuming that the saturated solutions behave ideally.

Experimental

Ethanol and methanol (anhydrous commercial products) were refluxed over silver oxide, distilled and dehydrated with magnesium by the method of Lund and Bjerrum.[8]

The density of each lot of alcohol treated in this way was determined in a 100-ml. pycnometer with which the density of a given sample could be checked to within ±3 units in the fifth decimal place. The water content of our methanol samples ranged from 0 to 0.03%, while that of ethanol varied from 0.01 to 0.07%. The specific conductance at 25° of the methanol varied from 2.9 to 5.0 $\times 10^{-6}$ cm.$^{-1}$ ohm^{-1}; the range in the corresponding values for ethanol was from 0.4 to 1.2 $\times 10^{-7}$ cm.$^{-1}$ ohm^{-1}. The conductance of the alcohol was subtracted from the observed specific conductance where necessary.

The acids used in this study were recrystallized and tested for purity.

The silver salts of the acids were precipitated from solutions of the corresponding sodium salts with a slight excess of silver nitrate. These precipitates were washed thoroughly and recrystallized from hot water. The coarsely crystalline products obtained in this way were washed with water, then with ethanol, and air dried.

Saturated solutions of these silver salts were prepared in conductance cells through which a stream of previously dried nitrogen, saturated with the vapor of the solvent, was led to provide stirring. When the conductance had become constant, samples of the saturated aqueous solutions were withdrawn and analyzed for silver by the Volhard method except in the case of salicylate and picrate, where the potentiometric method was used. The solubilities in ethanol and methanol were determined by the conductance method, except in the case of silver picrate solutions which were titrated potentiometrically with thiocyanate. The conductance cells were of the type used by Kolthoff and Willman.[9] Their cell constants were determined in the usual way.

Results

The solubilities of the silver salts in methanol and ethanol were computed from the specific conductances of the saturated solutions by the successive approximation method. For these computations it was necessary to know the equivalent conductance of the ions of each silver salt at the concentrations in the saturated solutions. These values were obtained from the equivalent conductances of the corresponding alkali salt, of silver nitrate or perchlorate, and of the alkali nitrate or perchlorate by means of the Kohlrausch relation

$$\Lambda_{AgA} = \Lambda_{NaA} + \Lambda_{AgNO_3} - \Lambda_{NaNO_3}$$

The required values for the alkali salts in ethanol were taken from the work of Goldschmidt,[10] and those for silver nitrate, silver perchlorate, alkali nitrates, and alkali perchlorates in ethanol from the data of Barak and Hartley.[11] The necessary data for the alkali nitrates and silver nitrate in methanol were taken from the results of Frazer and Hartley,[12] and those for sodium salicylate in methanol from the measurements of Goldschmidt and Aas.[13]

There are no data in the literature for the conductances of the alkali nitrobenzoates and benzoates in methanol; accordingly, they were measured in this study. These results are given in Table I.

TABLE I

EQUIVALENT CONDUCTANCE OF SOME ALKALI SALTS IN METHANOL AT 25°

Concn. $m \times 10^4$	Potassium *o*-nitrobenzoate	Potassium *m*-nitrobenzoate	Potassium *p*-nitrobenzoate	Sodium benzoate
2.00	89.6	79.3	82.5	..
4.00	88.5	78.7	81.6	78.2
6.00	87.7	78.3	81.0	77.9
8.00	87.1	77.9	80.5	77.6
10.0	86.5	77.5	80.1	77.0
12.0	..	..	..	75.8
14.0	..	..	..	75.4
16.0	85.0	76.7	78.7	75.1
20.0	84.1	75.8	77.9	74.4

The solubilities of the silver salts were computed by assuming, as a first approximation, that the equivalent conductances of the ions in the saturated solutions were the same as at infinite dilution. Using the approximate value of the solubility so obtained, the values of the equivalent

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[7] A. Macfarlane and H. Hartley, *Phil. Mag.*, **13**, 425 (1932); **20**, 611 (1935).

[8] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[9] I. M. Kolthoff and A. Willman, THIS JOURNAL, **56**, 1008 (1934).

[10] H. Goldschmidt, *Z. physik. Chem.*, **99**, 116 (1921).

[11] M. Barak and H. Hartley, *ibid.*, **A165**, 272 (1933).

[12] J. E. Frazer and H. Hartley, *Proc. Roy. Soc.* (London), **A109**, 351 (1925).

[13] H. Goldschmidt and F. Aas, *Z. physik. Chem.*, **112**, 423 (1924).

Table II

Solubilities of Several Silver Salts in Water, Methanol, and Ethanol at 25°

Silver salt	Sp. cond. × 10^6 Methanol	Sp. cond. × 10^6 Ethanol	Solubility Water	Solubility Methanol	Solubility Ethanol	$D_{Ag}D_A$ Water–Methanol	$D_{Ag}D_A$ Water–Ethanol
Benzoate	5.77	0.79	0.0162[a]	0.000723	0.000237	259	2410
o-Nitrobenzoate	15.9	2.05	.0426	.00204	.000653	437	4260
m-Nitrobenzoate	4.21	0.72	.00500	.000567	.000197	77	645
p-Nitrobenzoate	8.07	1.46	.00894	.00108	.000438	69	416
Salicylate	5.08	1.10	.00442	.000569	.000310	61	205
Picrate	..	73.4	.0475	.0354	.0349	1.80	1.85
(Iodate)	..	(0.0015)	.000177[b]	..	($< 10^{-6}$)	...	...

[a] I. M. Kolthoff and W. Bosch, *J. Phys. Chem.*, **36**, 1685 (1932).

[b] I. M. Kolthoff and J. J. Lingane, *ibid.*, **42**, 133 (1938).

conductances of the ions at that concentration were computed with the aid of the Kohlrausch rule. Successive approximations were made in this way until a constant value for the solubility was obtained. A summary of the results is given in Table II. The solubilities are given in moles per liter.

In order to compute the ionization constants of the acids in methanol and ethanol from those in water by means of equation (6), it was necessary to know the distribution coefficients of the uncharged acids. Also, for comparison of the calculated and observed values of the ionization constants in the alcohols, it was necessary to have directly determined values of these constants in the alcohols. The required data are available in the literature, except the solubilities and dissociation constants of the three nitrobenzoic acids in methanol.

These solubilities were determined by titrating samples of the saturated solutions, after dilution with water, with standard baryta solution, using phenolphthalein as indicator.

Bright and Briscoe[14] determined the acidity constants of the nitrobenzoic acids in water–methanol mixtures, and extrapolated the values to 100% methanol. These constants given by Bright and Briscoe, together with the value of the ionization constant of benzoic acid in Table IV, give 7.4, 8.0, and 8.1, respecitvely, for the values of pK for *o*-, *m*- and *p*-nitrobenzoic acids. Since the extrapolation involves an uncertainty, and the measurements involve an interphase potential, the ionization constant of *o*-nitrobenzoic acid was determined by us by the conductivity method. The calculation was made in the classical way by means of the Ostwald dilution formula. Since the ionic strength of the solutions was very small, no correction was applied for the activity of the ions.[15]

For the calculation of the degree of dissociation, α, values of the equivalent conductance of the acid at infinite dilution were calculated in the usual way from conductance data for the potassium salt of the acid (Table I), hydrochloric acid,[16] and potassium chloride.[17] The values obtained are given in Table III. The average value of K of 6×10^{-8} or a pK of 7.22 corresponds reasonably well with the value 7.4 computed from the acidity data of Bright and Briscoe. In Table III, κ is the specific conductance, Λ the equivalent conductance, and α the degree of dissociation.

Table III

Ionization Constant of *o*-Nitrobenzoic Acid in Methanol at 25°

Concn. (molar)	$\kappa \times 10^5$	Λ	$\alpha \times 10^4$	$K \times 10^8$
0.1520	1.76	0.116	6.4	6.2
.1025	1.44	.140	7.7	6.1
.0755	1.19	.158	8.7	5.8
				Average 6.0

A summary of the solubility and ionization constant data for the various acids at 25° in water, methanol, and ethanol is given in Table IV. The solubilities, s, are given in moles per liter of solution. K represents the ionization constant.

With these data it is possible to compute pK values for the several acids in methanol and ethanol by means of equation (6), and to compare them with the experimental values. The results are given in Table V. The data needed for the calculations are given in the previous tables. The distribution coefficients of the un-ionized part of

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[14] W. L. Bright and H. T. Briscoe, *J. Phys. Chem.*, **37**, 787 (1933).

[15] (a) M. S. Sherrill and A. A. Noyes, This Journal, **48**, 1861 (1926); (b) M. Randall and C. F. Failey, *Chem. Rev.*, **4**, 291 (1927).

[16] D. M. Murray-Rust and H. Hartley, *Proc. Roy. Soc.* (London), **A126**, 84 (1929).

[17] G. Carrara, *Gazz. chim. ital.*, **26**, I, 119 (1896).

TABLE IV

IONIZATION CONSTANTS AND SOLUBILITIES OF SEVERAL ACIDS IN WATER, METHANOL, AND ETHANOL AT 25°

Acid	Water		Methanol		Ethanol	
	S	$K \times 10^4$	S	$K \times 10^9$	S	$K \times 10^9$
Benzoic	0.0279[a]	0.661[a]	3.16[f]	0.379[h]	2.91[e]	0.037[h]
o-Nitrobenzoic	.0442[a]	61.2[a]	2.99[g]	60[g]	2.81[b]	3.8[b]
m-Nitrobenzoic	.0204[b]	3.38[b]	3.46[g]	10[k]	3.50[b]	0.673[h]
p-Nitrobenzoic	.0016[b]	3.98[b]	0.200[g]	7.95[k]	0.138[b]	1.2[b]
Salicylic	.0160[a]	10.6[a]	2.57[f]	13.2[h]	2.31[b]	2.2[h]
Picric	.0578[c]	1600[d]	0.628[g]	155000[i]		175000[j]

[a] Ref. 15b. [b] Ref. 6. [c] "International Critical Tables," Vol. IV, 1928, p. 253. [d] I. M. Kolthoff, "Sāure–Basen Indicatoren," Verlag von J. Springer, Berlin, 1932. [e] A. Seidell, "Solubilities of Inorganic Compounds," Vol. I, D. Van Nostrand, New York, N. Y., 1919, p. 134. [f] Results obtained by L. S. Guss in this Laboratory. [g] Results obtained by the authors. [h] Goldschmidt and Mathiesen, *Z. physik. Chem.*, **119**, 439 (1926). [i] Goldschmidt and Aarflot, *ibid.*, **117**, 312 (1925). [j] Goldschmidt, *Z. physik. Chem.*, **91**, 46 (1916). [k] Computed from the measurements of Bright and Briscoe, ref. 14. L. S. Guss in the laboratory found 25×10^{-9} for the ortho-, 5.0×10^{-9} for the meta- and 4.0×10^{-8} for the *p*-nitrobenzoic acid.

TABLE V

IONIZATION CONSTANTS IN METHANOL AND ETHANOL FROM DISTRIBUTION DATA

Acid	D_HD_A	D_{HA}	pK'	pK'' calcd.	pK'' exptl.
		Ethanol			
Benzoic	17350	0.00914	4.2	10.4	10.4
o-Nitrobenzoic	30600	.0109	2.2	8.7	8.4
m-Nitrobenoic	4640	.00500	3.5	9.5	9.2
p-Nitrobenzoic	2990	.00720	3.4	9.0	8.9
Salicylic	1475	.00537	3.0	8.4	8.7
Picric	13.3		0.8		3.8
		Methanol			
Benzoic	1050	0.00841	4.2	9.3	9.4
o-Nitrobenzoic	1770	.0103	2.2	7.4	7.2–7.6
m-Nitrobenzoic	315	.00514	3.5	8.3	8.0–8.3
p-Nitrobenzoic	280	.00480	3.4	8.1	8.1–8.4
Salicylic	247	.00482	3.0	7.7	7.9
Picric	7.3	.0210	0.8	3.5	3.8

the acids, D_{HA}, were computed from the solubility data for the acids, assuming that the activity coefficients for the uncharged molecules were unity in all three solvents. The values of D_{HA} in water were corrected for the amount of dissociation. The values of D_HD_A needed for these calculations were obtained by multiplying the values of $D_{Ag}D_A$ given in Table II by D_H/D_{Ag}. These latter values were computed from the standard electrode potentials of silver in the three solvents by means of equation (5). In water, the value 0.7996 v.[18] for the electrode potential of silver and the values 0.764[7] v. and 0.749[7] v. in methanol and ethanol, respectively, were used. The values 3.99 and 7.15 for D_H/D_{Ag} were found for water–methanol and water–ethanol, respectively.

Discussion.—From the results in Table V it is seen that the calculated values of *pK* are in fair agreement with the experimentally determined ones. The differences between the two are no larger than the uncertainties in the experimentally determined constants and in the various assumptions and approximations which have been made. The agreement is of the same order as that obtained by Bjerrum and Larsson[6] in ethanol.

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Summary

It has been pointed out that the product and the quotient of the distribution coefficients of ions between two solvents can be determined in an exact way. When these values are known it is possible to calculate equilibrium constants in one solvent from the known values in water.

The ionization constants of six acids in methanol and ethanol were calculated from distribution data and the values of the constants in water. The values calculated in this way were found to be in fair agreement with the experimentally determined ionization constants in methanol and ethanol.

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[18] J. J. Lingane and W. D. Larson, THIS JOURNAL, **58**, 2647 (1936).