NOMENCLATURE

g = acceleration due to gravity, 980.1 cm. per sec.^{2}
h = capillary height, cm.
r = capillary radius, cm.
γ = surface tension, dynes per cm. or (newton per meter) × 10^3
ρ = density of the liquid, grams per cm.^{2}
Δ = difference of two quantities

LITERATURE CITED

(1) Richards, T.W., Coombs, L.B., *J. Am. Chem. Soc.* **37**, 1656 (1915).
(2) Scatchard, G., Wood, S.E., Mochel, J.M., *J. Phys. Chem.* **62**, 712 (1940).
(3) Sugden, S., *J. Chem. Soc. (London)* **119**, 1483 (1921).
(4) Timermans, J., "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions," Vol. 1, p. 452, Interscience, New York, 1960.
(5) *Ibid.*, p. 817.

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Salting Effects in Several Alcohol-Electrolyte-Water Systems

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Salting effects of sodium sulfate, potassium fluoride, potassium chloride, sodium perchlorate, and perchloric acid on cyclohexanol, 1-pentanol, and 1-butanol were determined by measuring the solubilities of the alcohols in the various electrolyte solutions. Solubilities were determined by color development and spectrophotometry. The relevant Setschenow parameters are reported. There was no apparent correlation between the salting effect and the dipole moment of the alcohol.

DATA on the salting effect of various electrolytes on several alcohols in aqueous solution were obtained during studies of the competitive adsorption of alcohols and salts at the dropping mercury electrode. To make meaningful comparisons, the activity coefficients of the alcohols were calculated from the solubilities of each alcohol in the various electrolyte solutions used. Since these data could be of use in other investigations, they are separately reported here together with details of the method used, which appears to be applicable to the range of alcohols.

"Salting effect" refers to the increase or decrease in the activity coefficient of the dissolved alcohol in the presence of a salt; an increased coefficient corresponds to salting out, a decreased coefficient in salting in. The activity coefficients are related to the solubilities of the alcohol by

$$fS = f^\circ S^\circ \qquad (1)$$

where S° and S are the solubilities of the alcohol in pure water and in the salt solution, respectively, and f° and f are the corresponding activity coefficients. Taking the activity coefficient in pure water as unity, one obtains

$$f = S^\circ / S \qquad (2)$$

Strictly speaking, the activity coefficient so defined refers only to a saturated solution of the alcohol. However, the variation of the activity coefficient of a nonelectrolyte with changing concentration of the nonelectrolyte is small compared to the salting effect, and consequently we refer to the coefficient defined by Equation 2 as "the" activity coefficient of the alcohol in the relevant salt solution.

Solubility determinations and calculations according to Equation 2 were performed for 1-butanol, 1-pentanol, and cyclohexanol in solutions of potassium fluoride, potassium chloride, sodium sulfate, sodium perchlorate, and perchloric acid; the concentrations of the electrolytes ranged from 0.1 to 1.4M. Previous workers have generally found that the logarithm of the activity coefficient of the nonelectrolyte is a linear function of the electrolyte concentration—i.e.,

$$\log f = KC_s \qquad (3)$$

where C_s is the electrolyte concentration in moles per liter of solution and K, the Setschenow parameter, is a constant for a given alcohol and a given electrolyte. We found this relationship to hold for all systems studied. Values of the Setschenow parameters obtained are shown in Table I.

The salting effect of a given electrolyte is essentially the same toward 1-pentanol and cyclohexanol, except perhaps in perchlorate solutions, whereas there is an appreciable difference with 1-butanol. The molar solubilities of the alcohols in distilled water are: 1-pentanol, 0.243; cyclohexanol, 0.389; 1-butanol, 1.01.

Nonpolar nonelectrolytes have been used in recent studies of salting-out—and, more rarely, salting-in—effects. Examples are benzene (*5*) and hydrogen (*6*). However, dipole moments and salting effects observed in potassium chloride solutions have been compared; it seemed that the

Table I. Setschenow Parameters for Several Alcohols in Aqueous Electrolytes

(24.5° ± 0.5° C.)

Electrolyte in Solution[a]	Alcohol		
	1-Pentanol	Cyclohexanol	1-Butanol
Na_2SO_4	0.610[b]	0.596[b]	0.561
KF	0.301	0.319[b]	0.287
KCl	0.215	0.222	0.178
$NaClO_4$	0.14[c]	0.125[c]	0.084
$HClO_4$	–0.096[c]	–0.033[c]	–0.153

[a] Three concentrations of electrolyte used, except where otherwise indicated. [b] Four concentrations. [c] One concentration.

extent of salting out decreases with increasing dipole moment (*3*). Apparently, no recent comparison has been made of the salting effects shown by various electrolytes toward nonelectrolytes which have large but similar dipole moments. In this respect, the values in Table I should be of interest; the alcohol dipole moments (in benzene, at 25° C.) are (*4*): 1-butanol, $\mu = 1.63D$; 1-pentanol, $\mu = 1.66D$; cyclohexanol, $\mu = 1.9D$. While there is evidently no direct correlation between nonelectrolyte dipole moment and the salting effect in these systems, the magnitude of the salting effect in aqueous solutions generally depends on the ionic species present in solution (*5*). This fact has been related to hydration of the ions and a corresponding decrease in water activity (*2*). The apparent absence of a direct correlation between alcohol dipole moment and the Setschenow parameter emphasizes the importance of water-ion interactions in aqueous salting effects.

EXPERIMENTAL

Molar, $0.5M$, and $0.1M$ electrolyte solutions were saturated with an alcohol during 30 minutes of vigorous mechanical shaking with an excess of the alcohol. After shaking, the solutions were set aside for several hours, or until the aqueous layers became clear. During and after shaking, the solutions remained in glass-stoppered flasks. The temperature of the solutions remained within the range 24–25° C. Samples were prepared from the equilibrated solutions as follows.

1-Pentanol (and cyclohexanol) solutions: 1-ml. aliquots from 1-pentanol solution (0.5-ml. aliquots from cyclohexanol solution) were diluted to 250 ml. with distilled water. 1-ml. portions of the diluted solutions were transferred to dry test tubes.

1-Butanol solutions: A microliter syringe was used to transfer 10-μl. aliquots from the saturated solutions into 1-ml. volumes of distilled water in test tubes.

Precautions were taken to prevent undissolved alcohol from being transferred along with the aliquots taken from the saturated solutions.

Standard solutions of the alcohol in water were prepared volumetrically. Samples were prepared from the standard solutions as described above.

Color was developed in each tube by a method similar to that described by Boruff (*1*) for the spectrophotometric determination of fusel oil. It was necessary to modify the accepted method by lengthening the times allowed for the first two steps in the procedure—i.e., addition of the reagents to the samples—to accommodate a large number of samples and standards at one time. The reagents were those called for by Boruff (*1*): (I) a solution of *p*-dimethylaminobenzaldehyde (1 gram per 100 ml.) in dilute (approximately 5%) sulfuric acid, and (II) concentrated sulfuric acid, added to the tubes in the prescribed order and amounts. The *p*-dimethylaminobenzaldehyde was supplied by Eastman Organic Chemicals; reagent grade sulfuric acid was used. The tubes were cooled in an ice bath before and during addition of the reagents. Color development was then accomplished by immersing each tube in a boiling-water bath for a timed interval (1-pentanol and cyclohexanol, 20 minutes; 1-butanol, 30 minutes). At the end of this period, each tube was transferred to an ice bath and, afterward, returned to room temperature.

Per cent transmittance of each developed solution was measured at 535 mμ, using a Spectronic 20 spectrophotometer. Preliminary tests indicated obedience to Beer's law, despite the modifications already mentioned.

The per cent transmittance values for standards were plotted on semilog graph paper *vs.* alcohol concentration. The line of best fit was drawn and the alcohol concentration in the saturated solutions was found by graphical interpolation.

Because of dilution of the electrolyte solutions by dissolved alcohol, it was necessary to correct the original values of the electrolyte molarity. Experiments with 1-butanol and cyclohexanol indicated that the solutions were diluted by a volume approximately equal to the volume of alcohol dissolved. Exact dilution factors were not determined because saturation of the solutions could be obtained only after extensive shaking. Instead, the factor $(100 - s)/100$, was multiplied by the original electrolyte concentrations, where s is the volume of alcohol dissolved in 100 ml. of alcohol-electrolyte-water solution.

LITERATURE CITED

(1) Boruff, C.S., *J. Assoc. Offic. Agr. Chemists* **42**, 331 (1959); **44**, 383 (1961).

(2) Conway, B.E., Desnoyers, J.E., Smith, A.C., *Phil. Trans. Roy. Soc. (London)* **A256**, 389 (1964).

(3) Long, F.A., McDevit, W.F., *Chem. Rev.* **51**, 119 (1952).

(4) McClellan, A.L., "Tables of Experimental Dipole Moments," pp. 124, 154, 215, Freeman, San Francisco, 1963.

(5) McDevit, W.F., Long, F.A., *J. Am. Chem. Soc.* **74**, 1773 (1952).

(6) Ruetschi, P., Amlie, R.F., *J. Phys. Chem.* **70**, 718 (1966).

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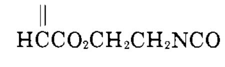
CORRECTION

In the article "Selective Hydrogenation of the Double Bond in Unsaturated Aliphatic Isocyanates," by R. J. Knopf [J. CHEM. ENG. DATA **15**, 196 (1970)], there are two errors in Table I, page 198.

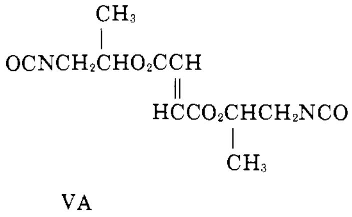
Structure IVA should read



$$\begin{array}{l} \mathrm{OCNCH_2CH_2O_2CCH} \\ \qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\quad \mathrm{HCCO_2CH_2CH_2NCO} \end{array}$$

IVA

Structure VA should read



$$\begin{array}{l} \qquad\qquad \mathrm{CH_3} \\ \qquad\qquad | \\ \mathrm{OCNCH_2CHO_2CCH} \\ \qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\quad \mathrm{HCCO_2CHCH_2NCO} \\ \qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad \mathrm{CH_3} \end{array}$$

VA