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Properties of Organic-Water Mixtures. I. Activity Coefficients of Sodium Chloride, Potassium Chloride, and Barium Nitrate in Saturated Water Mixtures of Glycol, Glycerol, and Their Acetates. Model Solutions for Hyperfiltration Membranes¹

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The solubility of NaCl in mixtures of water with ethylene glycol, its mono- and diacetates, glycerol, and its mono-, di-, and triacetates was determined at 25° by packed column techniques. The solubilities of KCl and Ba(NO₃)₂ were determined for water mixtures of glycol, glycerol, and the corresponding fully acetylated compounds. Miscibility limits were established in the presence and absence of salts. From the solubility data, activity coefficients $\gamma_{\pm(0)}$ of the salts were computed using the same reference states as for aqueous solutions and expressing concentrations in moles/kg. of water. While the values of $\gamma_{\pm(0)}$ in the glycol- and glycerol-water mixtures were usually less than for the two-component aqueous solutions, they increased with the fraction of hydroxyl groups acetylated and were more than 1000 times larger for the fully acetylated compounds at low water content. Some of the implications of these results for hyperfiltration with membranes are discussed.

To understand better the organic membranes used in hyperfiltration (separation of salts from water by filtration under pressure) it seemed desirable to obtain thermodynamic and transport data for a variety of organic-water mixtures. The present paper, the first one of a series, deals with the activity coefficients $\gamma_{\pm(0)}$ of NaCl, KCl, and Ba(NO₃)₂ in water-organic mixtures at saturation. The organic components are ethylene glycol (EG), glycerol (G), and their various acetates [ethylene glycol monoacetate (EGMA), ethylene glycol diacetate (EGDA), glycerol monoacetate (GMA), glycerol diacetate (GDA), glycerol triacetate (GTA)]. These compounds were selected because of their possible relevance to cellulose acetate membranes for which the acetates might be suitable model compounds. The solubility measurements were carried out by packed column techniques^{2,3} using radiometric methods of analysis whenever solubilities were low. Comparison of solubilities measured in packed columns with values in the literature and values obtained by shaking experiments showed that this method can be used even for highly soluble salts.

Experimental

1. **Packed Column Method.**—The packed column technique for measuring solubilities^{2,3} involves passage of a solution through a small column filled with salt and analysis of the effluent. Most of the columns were 6 mm. i.d.; for the tracer experiments 2 mm. i.d. columns were used. Salt beds were 6 to 8 cm. high. The columns were thermostated by circulation of water (25 ± 0.02°) through a jacket surrounding them. When solubilities were high the solutions were permitted to remain in contact with the salt bed for 5 to 10 min. and only the interstitial liquid was withdrawn. At low solubilities, where equilibration is very rapid, the solutions could be withdrawn continuously. Normally, gravity flow yielded adequate flow rates; for the more viscous solutions, however, a small external pressure was applied. For each solvent mixture at least two samples were collected and in many cases flow rates were varied to establish that sufficient contact time had been allowed.

The effluent samples were weighed and analyzed. At high solubility the salt concentration was established by titration. Chloride analyses were by titration with silver nitrate, using chromate as indicator. Barium analyses were by EDTA titrations using methyl thymol blue as indicator. Titration precision was usually better than 0.1%.

(1) Work performed for the Office of Saline Water, U. S. Department of the Interior, at the Oak Ridge National Laboratory, Oak Ridge, Tenn., operated by Union Carbide Corp for the U. S. Atomic Energy Commission.

(2) R. J. Raridon, Ph.D. Thesis, Vanderbilt University, *Dissertation Abstr.*, **20**, 118 (1959).

(3) K. A. Kraus, H. O. Phillips, and F. Nelson, "Radioisotopes in the Physical Sciences and Industry, Sept., 1960," Vol. III, IAEA, Vienna, 1962.

For the radiometric method the salts were prepared with a known amount of radiotracer per gram of salt. The weighed effluent samples were counted in a well-type scintillation counter; from the known specific activity of the salt the concentration of salt in the solution was then established. The counts were interspersed frequently with standards, particularly in the case of sodium and potassium where essentially simultaneous counting of standards simplified correction for decay.

2. **Tracers.**—The radioactive tracers Na²⁴ ($T_{1/2}$ = 15 hr.), K⁴² ($T_{1/2}$ = 12.5 hr.), and Ba¹³³ ($T_{1/2}$ = 10.7 years) were obtained from the Radioisotopes Division of ORNL. These tracers were of high specific activity (from 0.2 to 1.3 curies per g. of element) and had stated radiochemical purities greater than 98%. No further purifications were carried out. The radiochemical purities of Na²⁴ and K⁴² were checked by decay measurements, while Ba¹³³ was checked by γ -scintillation spectrometry. The Ba¹³³ tracer was evaporated to dryness several times with concentrated HNO₃ to remove traces of chloride.

3. **Materials.** (a) **Salts.**—Reagent grade salts were used, with the following stated maximum impurities: NaCl, 0.025%; KCl, 0.04%; Ba(NO₃)₂, 0.16%. The salts were dried at 400° for 24 hr. to remove traces of moisture.

(b) **Solutions.**—Mixtures of the organic solvents and water were prepared by weight; EGDA, GDA, and GTA are not completely miscible with water, particularly in presence of salts, and only mixtures containing small or moderate amounts of water could be used.

(c) **Organic Compounds.**—Ethylene glycol, glycol diacetate, glycerol, and glycerol triacetate were middle fractions (60–80%) obtained by distillation under reduced pressure of commercially available materials. Purity of the esters was established by measuring saponification equivalents and per cent hydroxyl; the fraction of unacetylated hydroxyl groups was less than 0.003.

Glycerol 1-monoacetate as prepared by the method of Baer and Fischer⁴ was a residue dried by pumping at 0.5 mm. and 35° for 3 hr. Based on periodate oxidation analysis, the material contained approximately 1% glycerol. Through combination of periodate oxidation and determination of the saponification equivalent, the monoacetate content was shown to be greater than 98.5%.

Ethylene glycol monoacetate was prepared from a commercial mixture (22% glycol, 61% monoacetate, 17% diacetate) through batch countercurrent solvent extraction with chloroform; 55 g. of the glycol acetate mixture was treated with 100 ml. of chloroform and 25 ml. of water in the first stage. The chloroform layer was then extracted with water (25 ml.) and the aqueous layer with chloroform (100 ml.) through six additional stages. Through analysis of the various stages, distribution coefficients (concentration in the organic phase/concentration in the aqueous phase) were found to be approximately 0.003 for glycol, 0.4 for the monoacetate, and 10 for the diacetate. EGMA was isolated from stages 4 and 5; it had a boiling point of 45–47° at ca. 1 mm. pressure, a saponification equivalent weight of 105 (calculated 104), and n_D^{20} 1.4200. It contained 0.3% glycol as determined from periodate oxidation. The product contained 58% of the monoacetate of the original mixture.

(4) E. Baer and H. O. L. Fischer, *J. Am. Chem. Soc.*, **67**, 2031 (1945).

Glycerol diacetate (probably a mixture of 1,2- and 1,3-diacetates) was obtained from commercial diacetin (3% glycerol, 15% GMA, 43% GDA, 39% GTA) through a combination of solvent extraction techniques. A preliminary purification was carried out by extracting 433 g. of diacetin in 370 ml. of water three times with 370 ml. of diethyl ether each. This step removed over 90% of the triacetate and 42% of the diacetate. The aqueous phase was extracted three times with 185 ml. of chloroform and the combined chloroform layers were extracted four times with water (25-ml. portions). The chloroform layer was then evaporated; the residue contained 22% of the starting material and was 91% GDA, 8% GTA, with the remainder glycerol and monoacetate. Most of the residue (87 g.) was dissolved in a mixture of 100 ml. of water and 50 ml. of chloroform and subjected to countercurrent batch extraction through four stages using the same water-chloroform ratio. The final material was obtained from a combination of the organic phases of stages 2 and 3 and the aqueous phases of stages 3 and 4. After evaporating the solvent at reduced pressure (temperature < 45°) and final drying at 0.5 mm. pressure and 35° for 3 hr., there remained 60 g. of glycerol diacetate. As found through combination of periodate and saponification equivalent analyses, it contained less than 0.2% glycerol, and less than 0.3% monoacetate; the saponification equivalent was 88.3% (calculated 88.0%, n_{D}^{20} 1.4384).

4. Analytical Methods.—The miscibility limits of the acetates with water at 25° were determined by shaking mixtures in stoppered tubes in a constant temperature bath. Appropriate analyses were made for the various salts. The organic-rich phases were analyzed for water by Karl Fischer titrations (precision *ca.* 1%). The water-rich phases were analyzed for acetate (precision *ca.* 5%) by a semimicro adaptation of the standard saponification technique whereby back titration of excess alkali is performed on a boiling solution to minimize carbonate error, and in a flask under a reflux condenser to minimize loss of acetic acid.

Analysis for 1,2-glycols was carried out by the periodate oxidation method described by Allen, Charbonnier, and Coleman⁵ for the formic acid formed from glycerol, and the method of Kruty, Segur, and Miner⁶ for the titration of excess periodate. In the calculations it was assumed that ethylene glycol and glycerol 1-monoacetate react with 2 equivalents of periodate while glycerol reacts with 4 equivalents and yields formic acid.

Hydroxyl group determinations were carried out by the method of Freed and Wynne.⁷

Results and Discussion

1. Miscibility Limits.—Mixtures of water with ethylene glycol (EG), glycerol (G), ethylene glycol monoacetate (EGMA), or glycerol monoacetate (GMA) are miscible in all proportions even after saturation with NaCl, KCl, or Ba(NO₃)₂. Glycerol diacetate (GDA) was found to be miscible with water in all proportions. The system remained completely miscible after saturation with KCl or Ba(NO₃)₂; on saturation with NaCl, however, a miscibility gap appeared. The composition of the two phases is shown in Table I. Mixtures of water and ethylene glycol diacetate (EGDA) or glycerol triacetate (GTA) show a miscibility gap; this gap is increased on saturation with NaCl and KCl; Ba(NO₃)₂ seems to cause a slight salting in of the organic component in the water-rich phase but otherwise its effects are minor. Composition of the phases is shown in Table I.

Since at equilibrium the activity of water, a_1 , in the organic-rich phase is the same as in the water-rich phase, we may estimate the former through estimates of the latter. Values of a_1 in the saturated salt solutions are known for the two-component (salt-water) systems⁸

(5) N. Allen, H. Y. Charbonnier, and R. M. Coleman, *Anal. Chem.*, **12**, 384 (1940).

(6) M. Kruty, J. B. Segur, and C. S. Miner, Jr., *J. Am. Oil Chemists' Soc.*, **31**, 466 (1954).

(7) M. Freed and A. M. Wynne, *Anal. Chem.*, **8**, 278 (1936).

(8) $a_1(\text{NaCl})$ and $a_1(\text{KCl})$ from R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Academic Press, Inc., New York, N. Y., 1959;

TABLE I

EQUILIBRIUM MIXTURES OF ETHYLENE GLYCOL DIACETATE, GLYCEROL DIACETATE, AND GLYCEROL TRIACETATE WITH WATER AND SALTS (25°)

Salt	—Water-rich phase—		—Organic-rich phase—	
	Wt. % organic	Wt. % salt	Wt. % water	Wt. % salt
Ethylene glycol diacetate				
None	16	0	7.65	0
NaCl	1.8	25.7	2.72	<0.01
KCl	3.4	24.6	3.68	<.01
Ba(NO ₃) ₂	19	6.3	6.88	<.01
Glycerol diacetate				
NaCl	24	18	24	4.3
Glycerol triacetate				
None	7.4	0	4.60	0
NaCl	0.65	26.3	2.02	<0.01
KCl	1.2	25.7	2.59	<.01
Ba(NO ₃) ₂	7.3	8.4	4.27	<.01

$[a_1(\text{NaCl}) = 0.7528, a_1(\text{KCl}) = 0.8426, a_1(\text{Ba}(\text{NO}_3)_2) = 0.986]$. We may assume that, as a first approximation, addition of the organic materials to water or to the saturated solutions decreases a_1 essentially according to Raoult's law; we have computed it according to the equation

$$a_1 = a_1(\text{satd. aq. soln.}) \times \frac{n_{\text{H}_2\text{O}}}{(n_{\text{H}_2\text{O}} + n_{\text{org}})}$$

This yielded the estimated values of a_1 shown in Fig. 1. Included in this figure are also points for solutions saturated with MgCl₂; these are added because they extend measurements to very low values of a_1 . We have drawn a single curve for a_1 for the organic-rich phases of EGDA, and another one for GTA since there is presumably too little salt in the organic-rich phases to affect a_1 significantly. The curves describing a_1 in the organic-rich region are reasonably smooth and surprisingly similar for EGDA and GTA.

2. Solubility.—The solubilities of the various salts in the water-organic mixtures are summarized in Tables II to IV. The solubilities of NaCl and KCl in EG and G decrease less than an order of magnitude and in a uniform manner as the water content decreases. The solubilities of Ba(NO₃)₂ in these two solvents decrease little and show minima near 80% organic.

With EGDA and GTA, solubility of NaCl, KCl, or Ba(NO₃)₂ in the organic-rich phases is low and decreases dramatically with decreasing water content. The solubility of NaCl in EGMA, GMA, and GDA is intermediate between EG and G on the one hand and the completely acetylated compounds on the other.

Comparison of our measurements with those in the literature⁹⁻¹¹ were feasible only with EG and G. Agreement is satisfactory. The solubilities of NaCl and KCl in pure EG are 1-2% lower than those reported by Isbin and Kobe.¹⁰ Herz and Knoch¹¹ report values for NaCl and KCl in glycerol-water mixtures for a glycerol

$a_1(\text{Ba}(\text{NO}_3)_2)$ calculated from osmotic coefficients given by Robinson and Stokes but extrapolated to the saturated solution.

(9) A. Seidell; W. F. Linke, "Solubilities of Inorganic and Metal Organic Compounds," 4th Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1958.

(10) H. S. Isbin and K. A. Kobe, *J. Am. Chem. Soc.*, **67**, 464 (1945).

(11) W. Herz and M. Knoch, *Z. anorg. Chem.*, **45**, 263 (1905).

TABLE II

SOLUBILITY OF SOME SALTS IN WATER MIXTURES OF GLYCOL AND GLYCEROL (25°)

Wt. % organic	Solubility, g./kg. of mixed solvent		
	NaCl	KCl	Ba(NO ₃) ₂
	Ethylene glycol		
0.0	360.0	360.0	102.6
25.06	260.2	241.9	77.4
50.14	177.2	152.2	67.1
75.06	112.4	88.3	66.7
85.08	90.8	70.0	69.6
95.09	75.5	56.5	72.7
99.97	70.0	51.3	76.0
	Glycerol		
22.69	284.7	265.3	88.2
50.10	191.0	176.0	75.1
75.07	122.6	109.2	70.0
85.18	100.8	87.7	69.0
94.97	83.6	70.9	69.3
99.84	76.0	64.2	69.8

TABLE III

SOLUBILITY OF SOME SALTS IN WATER MIXTURES OF ETHYLENE GLYCOL DIACETATE AND GLYCEROL TRIACETATE (25°)

Wt. % organic	Solubility, g./kg. of mixed solvent		
	NaCl	KCl	Ba(NO ₃) ₂
	Ethylene glycol diacetate		
94.27			3.45 × 10 ⁻²
94.95			1.95 × 10 ⁻²
95.58			1.01 × 10 ⁻²
96.59			3.8 × 10 ⁻³
97.58	1.45 × 10 ⁻²	8.6 × 10 ⁻³	1.0 × 10 ⁻³
98.44	2.8 × 10 ⁻³	2.4 × 10 ⁻³	3.0 × 10 ⁻⁴
99.21	3.3 × 10 ⁻⁴	5.2 × 10 ⁻⁴	5.0 × 10 ⁻⁵
99.98	7.5 × 10 ⁻⁵	8.5 × 10 ⁻⁵	
	Glycerol triacetate		
95.92			9.0 × 10 ⁻³
96.76			3.4 × 10 ⁻³
97.46			1.4 × 10 ⁻³
98.00	6.7 × 10 ⁻³	5.2 × 10 ⁻³	5.8 × 10 ⁻⁴
98.50	2.1 × 10 ⁻³	2.1 × 10 ⁻³	
99.00	5.0 × 10 ⁻⁴		5.6 × 10 ⁻⁵
99.37	1.6 × 10 ⁻⁴	3.3 × 10 ⁻⁴	
99.95		8.6 × 10 ⁻⁵	

with stated impurity of ca. 1.5%. If this impurity is assumed to be water, the agreement is good.

3. Activity Coefficients.—For computation of activity coefficients $\gamma_{\pm(0)}$ of the salts in the water-organic mixtures, we shall select the same reference states as for solutions of the salts in water. At saturation the activity of the salt a_2 is thus the same for the water-salt (two-component) system as for the mixed solvent systems. Hence

$$a_2 = m_{+(aq)}^{\nu+} m_{-(aq)}^{\nu-} \gamma_{\pm(aq)}^{\nu} = m_{+(0)}^{\nu+} m_{-(0)}^{\nu-} \gamma_{\pm(0)}^{\nu} \quad (1)$$

where m is concentration at saturation, γ_{\pm} is the mean activity coefficient, and $\nu = \nu_+ + \nu_-$ is the number of moles of ions per mole of salt. Subscript (aq) refers to the water-salt (two-component) systems and subscript (0) to the three-component systems. We shall express concentrations m in terms of moles per kg. of water for both the two- and three-component systems. If $S_{(aq)}$

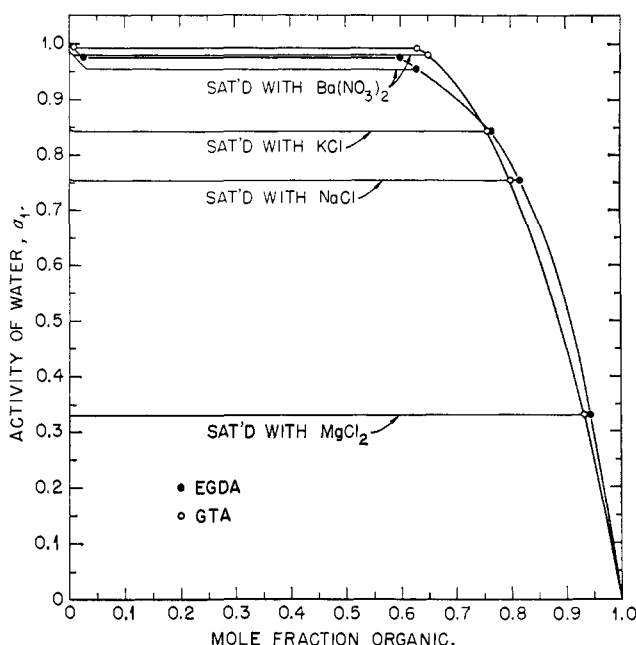


Fig. 1.—Activity of water in solutions saturated with salts and glycol diacetate or glycerol triacetate.

and $S_{(0)}$ are the solubilities in the two media in moles per kg. of solvent and f_w is the fractional water content of the water-organic mixture (kg. of water per kg. of solvent), $\gamma_{\pm(0)}$ is given by

$$\gamma_{\pm(0)} = \gamma_{\pm(aq)} S_{(aq)} f_w / S_{(0)} \quad (2)$$

With our selection of these concentration units for the mixed solvents,¹² $\gamma_{\pm(0)}$ must go to zero when the water

TABLE IV

SOLUBILITY OF NaCl IN SOME ACETATE-WATER MIXTURES (25°)

Wt. % organic	Solubility, g./kg. of mixed solvent	Activity coefficient $\gamma_{\pm(0)}$
Ethylene glycol monoacetate		
24.93	242.4	1.12
49.82	136.0	1.33
74.78	46.62	1.94
84.66	21.44	2.54
94.69	5.68	3.18
99.68	1.49	...
Glycerol monoacetate		
24.91	251.3	1.08
59.86	155.08	1.16
74.84	74.4	1.21
84.72	49.6	1.09
94.65	29.1	0.62
99.65	20.8	...
Glycerol diacetate		
77.90	38.8	2.06
86.05	15.5	3.23
94.93	1.74	10.4
99.91	0.12	...

(12) With the more "usual" concentration units, moles per kg. of solvent, the activity coefficient $\gamma_{\pm(0)}$ would be given by $\gamma_{\pm(0)}' = \gamma_{\pm(aq)} S_{(aq)} / S_{(0)} = \gamma_{\pm(0)} / f_w$.

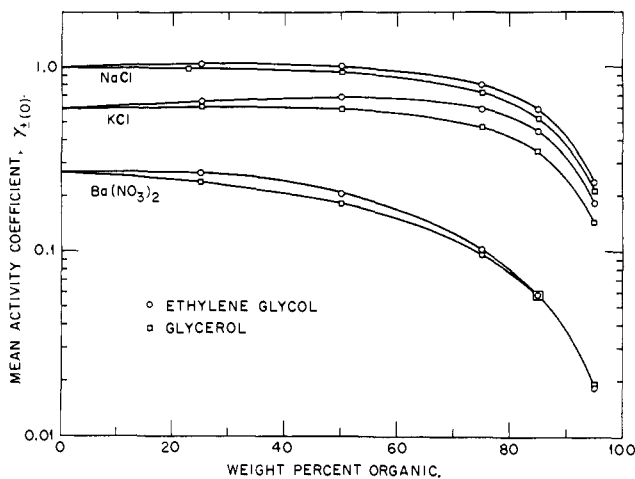


Fig. 2.—Activity coefficients in glycol- and glycerol-water mixtures.

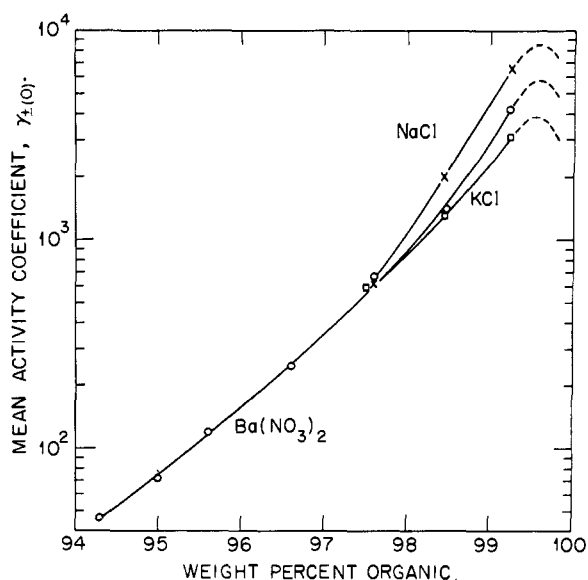


Fig. 3.—Activity coefficients in glycol diacetate-water mixtures.

content of the solvent goes to zero. In spite of this difficulty, selection of these concentration units appears desirable for our purposes since $\gamma_{\pm(0)}/\gamma_{\pm(aq)}$ will measure a relative selectivity of the medium for salt and water.

In the computation of $\gamma_{\pm(0)}$ we have taken $\gamma_{\pm(aq)}$ as 1.006, 0.588, and 0.266 for the saturated aqueous solutions of NaCl, KCl, and $\text{Ba}(\text{NO}_3)_2$, respectively. These values were obtained by extrapolation to saturation of data given in Harned and Owen.¹³

The activity coefficients $\gamma_{\pm(0)}$ computed from the solubility data are shown in Fig. 2-5. For acetates with miscibility gaps, activity coefficients are given only for the organic-rich phases; for the water-rich phases they did not differ much from $\gamma_{\pm(aq)}$.

For any given salt, values of $\gamma_{\pm(0)}$ in glycol- and glycerol-water mixtures (Fig. 2) are very similar.

(13) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958. It should be noted, however, that the value of $\gamma_{\pm} \approx 1.006$ used here for NaCl at saturation [based on the work of R. A. Robinson, *Trans. Roy. Soc. New Zealand*, **75**, 203 (1945)] differs markedly from the value $\gamma_{\pm} = 1.026$ given by G. Scatchard, W. J. Hamer, and S. E. Wood, *J. Am. Chem. Soc.*, **60**, 3061 (1938).

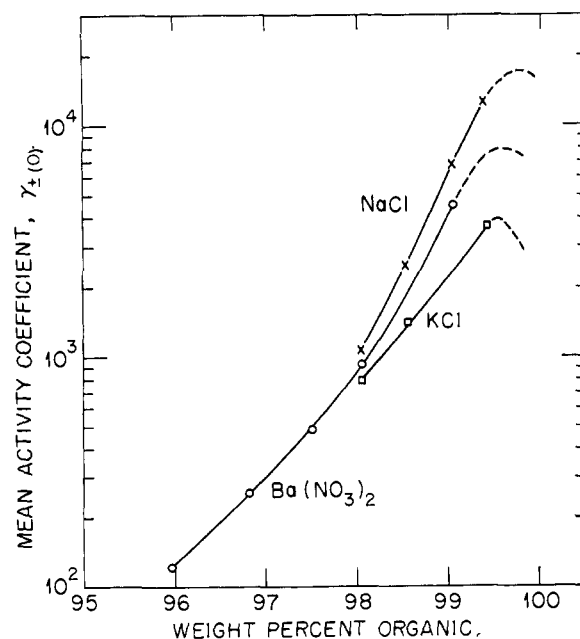


Fig. 4.—Activity coefficients in glycerol triacetate-water mixtures.

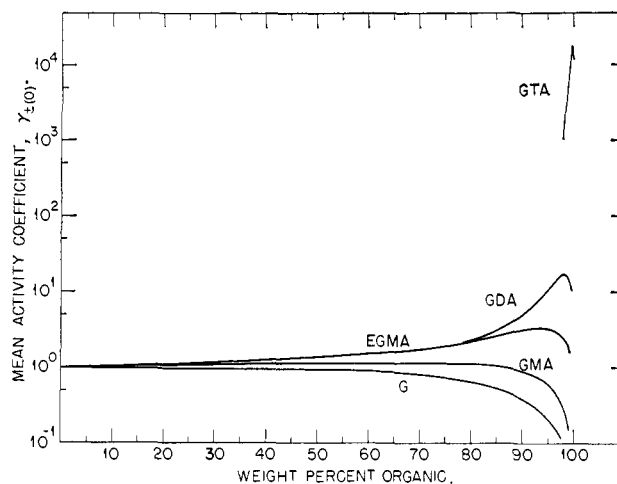


Fig. 5.—Activity coefficients of NaCl in water mixtures of glycerol, glycerol mono-, di-, and triacetate, and ethylene glycol monoacetate.

Further, $\gamma_{\pm(0)}$ of NaCl and KCl varies little with composition up to 60 weight % organic; at higher organic content, $\gamma_{\pm(0)}$ decreases rapidly. Activity coefficients of $\text{Ba}(\text{NO}_3)_2$ are similar, although the decrease becomes significant at somewhat lower organic content than for NaCl and KCl.

The activity coefficients in glycol diacetate (Fig. 3) and glycerol triacetate (Fig. 4) differ drastically from those in glycol and glycerol but they are very similar to each other. At low water content the activity coefficients become extremely large (ca. 10^3 at 98% organic); they are surprisingly independent of the type of salt used.

Activity coefficients of NaCl in glycerol and its acetates as well as in EGMA are compared in Fig. 5. The rapid increase in $\gamma_{\pm(0)}$ between 66 and 100% acetylation, which occurs at low water content, seems particularly noteworthy.

4. Glycol and Glycerol Acetate Solutions as Models for Hyperfiltration Membranes.—In recent years great interest has developed in hyperfiltration (or "reverse osmosis") in which salts are removed from water by forcing the salt solution through membranes which combine high salt rejection with reasonable transmission of water under moderate pressures. Cellulose acetate membranes cast under certain conditions were found to have these properties¹⁴; they can reject more than 95% of the salts from sea water and permit the purified water to go through the membrane at flow rates larger than 2 cm./hr. at 1500 p.s.i. applied pressure.

If we neglect interfacial effects, as seems reasonable,¹⁵ the effectiveness of membranes for separation of salts from water would presumably be determined either by the relative distribution of salts and water between the solution and the membrane phases or by differences in the relative transport properties (diffusion coefficients) of salts and water in the membrane phase or by a combination of both effects. Indeed, as will be discussed in another paper,¹⁶ when salt and water fluxes are closely coupled, the asymptotic rejection, R_∞ , at high flow rates will be determined by the relative distribution of salts and water between the membrane and solution phases. (Under these special and not unreasonable conditions $R_\infty = 1 - \gamma_{\pm(aq)}/\gamma_{\pm(0)}$.)

With uncharged membranes (*i.e.*, membranes not of the ion-exchange type) such as cellulose acetate membranes, forces effecting either a difference in distribution of salts and water or a difference in their relative transport properties must be of short range. The effective portion of such hyperfiltration membranes thus has substantially the properties of homogeneous aqueous-organic mixtures rather than of a porous body. Conversely, it should be possible to approximate some of the properties of membranes through study of appropriate water-organic solutions of appropriate water content. The organic compound in such "model solution" studies should be selected in such a manner as to reproduce as nearly as possible the characteristics of the membrane material. Of course, if a relation between model solutions and membrane behavior were established, selection of new membrane materials effective in hyperfiltration could come through such model solution studies; these in general are much simpler and less time consuming than the membrane studies and thus could serve for preliminary screening of suitable organic materials.

It seemed reasonable to select glycol and glycerol acetate solutions as models for cellulose acetate membranes. They should share with them some of the characteristic portions of the carbon skeleton as well as the multiple ester linkages.

We shall restrict ourselves here to an analysis of the equilibrium properties of these model systems and compare them with the equivalent properties of the membrane systems. As mentioned, hyperfiltration should be favored when the concentration of salt per 1000 g. of membrane water is substantially less than the molality of the contacting aqueous phase. In our terms this is equivalent to stating that the activity coefficients of the salt should be much higher in the membrane phase

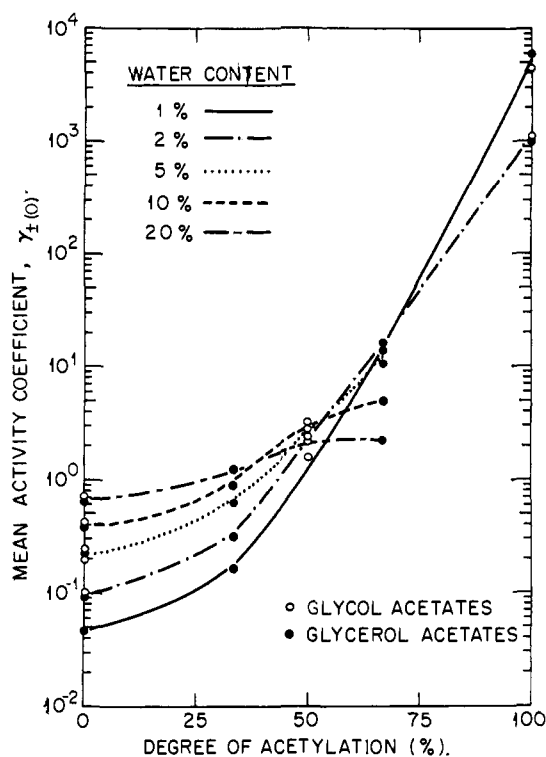


Fig. 6.—Activity coefficients of NaCl in water mixtures of glycol and glycerol acetates.

than in the aqueous phase. With the model system this would be equivalent to values of $\Gamma = \gamma_{\pm(0)}/\gamma_{\pm(aq)}$ much larger than unity. This ratio should of course be known as a function of salt activity or salt concentration in the aqueous phase. The present measurements of the model mixtures only yield Γ when the activity of salt equals that of the saturated solution. In all probability these values of Γ are lower limits when the solubilities are low, since then $\gamma_{\pm(0)}$ would either follow a Debye-Hückel relationship or reflect association; activity coefficients would rise on further dilution. For the more concentrated solutions the relationships are more complicated since activity coefficient minima may occur. However, even then it is unlikely that the ratio of $\gamma_{\pm(0)}$ at saturation to $\gamma_{\pm(0)}$ at the minimum is larger than the corresponding ratio of $\gamma_{\pm(aq)}$.

In the model glycol and glycerol acetate systems the activity coefficient $\gamma_{\pm(0)}$ of NaCl (at constant a_{NaCl}) is strongly dependent on water content and degree of acetylation. In Fig. 6 values of $\gamma_{\pm(0)}$ are given for various water contents (1 to 20%) as a function of the fraction F_{Ac} of hydroxyl groups acetylated. Interestingly, at any given water content, F_{Ac} seems to be the only important variable and $\gamma_{\pm(0)}$ seems insensitive to the type of compound used. This observation lends some confidence to the assumption that a similar relationship between activity coefficients and F_{Ac} is applicable to the various cellulose acetate derivatives. We note that very large values of $\gamma_{\pm(0)}$ can only be reached when F_{Ac} is large. Indeed, with $F_{\text{Ac}} < 0.6$, $\gamma_{\pm(0)}$ remains less than 10.

There is a striking dependence of $\gamma_{\pm(0)}$ on water content and high values are only attained at low water content. If one selects $\gamma_{\pm(0)}/\gamma_{\pm(aq)} = 50$ as a target number, since it would correspond to an asymptotic rejection rate of 98% in a system of closely coupled salt

(14) S. Loeb and F. Milstein, *Dechema Monograph.*, **47**, 707 (1962).

(15) G. Scatchard, *J. Phys. Chem.*, **68**, 1056 (1964).

(16) L. Dresner, J. S. Johnson, and K. A. Kraus, unpublished.

and water fluxes, one concludes from these model studies that the water content should be less than 5% for $F_{Ac} = 0.8$, which according to Loeb¹⁴ is a desirable degree of acetylation for membranes.

Since these conclusions on limits of acetylation and water content are deduced from activity coefficients at saturation, since $\gamma_{\pm(0)}$ for these systems would increase with dilution, and since $\gamma_{\pm(aq)}$, which for NaCl at saturation is *ca.* 1, will decrease with salt concentration in an intermediate range, some relaxation of the limits seems reasonable. We have also ignored here the case of poor coupling between water and salt fluxes where differences in diffusion coefficients could increase the asymptotic rejection of salt beyond that expected from the distribution coefficients alone. However, it seems unlikely that these differences would be large enough as to invalidate the principal conclusion—namely, that the effectiveness of existing cellulose acetate membranes must be caused by an effective layer which has a low water content.

We speak of an "effective layer" of the membranes because it is now almost certain that the cellulose acetate membranes, as a whole, are too thick to yield permeability of the type normally observed and at the same time be homogeneous enough to reject salt well. This observation has been made independently during the past year at a number of laboratories. We might mention here the work by Merten and co-workers¹⁶ which through electron microscopy showed existence of a thin, relatively homogeneous layer at the face of the membranes. It may be worthwhile here, however, to show that the same conclusion can be reached through analysis of the flux equations for water in a homogeneous membrane.

The diffusional flux of water J_1 (moles $\text{cm.}^{-1} \text{sec.}^{-1}$) through a membrane is described by

$$J_1 = \mathcal{D}_1 c_1 \nabla \mu_1 / RT \quad (3)$$

if the system does not contain other components which

(17) R. L. Riley, J. O. Gardner, and U. Merten, *Science*, **143**, 801 (1964).

can diffuse. In eq. 3, \mathcal{D}_1 is diffusion coefficient ($\text{cm.}^2 \text{sec.}^{-1}$), c_1 is concentration of water in the medium (moles cm.^{-3}), μ_1 is the chemical potential, R is the gas constant, and T is the absolute temperature. In a membrane system under pressure the chemical potential gradient of water (absence of salt) is given by

$$\nabla \mu_1 = V_1 \nabla p \quad (4)$$

where V_1 is molar volume and p is pressure. Since $c_1 = f_w \rho / M_1$, where f_w is the fractional water content, ρ is density of the solution, and M_1 the molecular weight of water

$$J_1 = \mathcal{D}_1 V_1 f_w \rho \nabla p / M_1 RT \quad (5)$$

For our system $V_1 \rho / M_1 \approx 1$. Hence, eq. 5 simplifies to

$$J_1 \approx f_w \mathcal{D}_1 \nabla p / RT \quad (5a)$$

For a membrane with thickness d of the homogeneous layer, $\nabla p = \Delta p / d$ and hence

$$d \approx f_w \mathcal{D}_1 \Delta p / J_1 RT \quad (6)$$

For a Loeb-type membrane which at 25° and an applied pressure of 100 atm. has a flow rate of 15 gal./ft.²/day

$$d \approx 1 \times 10^3 f_w \mathcal{D}_1 \quad (7)$$

If we assume $\mathcal{D}_1 = \text{ca. } 10^{-6}$, which seems reasonable for this type of membrane, then $d \approx f_w$ microns. From the data presented here we conclude that for such a membrane f_w is probably not much larger than 0.1 to 0.2. Hence the effective thickness of such a membrane is presumably of the order of 0.1 μ .

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Cyanogen Fluoride: Synthesis and Properties¹

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Monomeric FCN, b.p. -46° , has been prepared and isolated and its properties have been investigated. Of several successful high-temperature routes, pyrolysis of cyanuric fluoride at 1300° (50 mm.) is preferred and gives FCN in yields $>50\%$.

Although cyanogen fluoride, FCN, has been the subject of a number of investigations,² it apparently has not

(1) A preliminary communication of this work has been published: F. S. Fawcett and R. D. Lipscomb, *J. Am. Chem. Soc.*, **82**, 1509 (1960); see also R. D. Lipscomb and W. C. Smith, U. S. Patent 3,008,798 (1961); M. W. Farlow, U. S. Patent 2,980,739 (1961).

(2) (a) V. E. Cosslett, *Z. anorg. allgem. Chem.*, **201**, 75 (1931); (b) H. J. Callomon, H. W. Thompson, F. A. Anderson, and B. Bak, *J. Chem. Soc.*, 3709 (1953); (c) A. A. Woolf, *ibid.*, 252 (1954); (d) E. E. Aynsley, R. E. Dodd, and R. Little, *Proc. Chem. Soc.*, 265 (1959); (e) W. Hüchel, *Nachr. Akad. Wiss. Göttingen*, 36 (1946); *Chem. Abstr.*, **43**, 6793 (1949); (f) O. Ruff, *Ber.*, **69**, 193 (1936); (g) V. Migrdichian, "The Chemistry of Organic Cyano-

previously been isolated, in contrast with the other well-known cyanogen halides. In the present work,¹ it has been found that high-temperature pyrolysis of cyanuric fluoride, $(\text{FCN})_3$, under reduced pressure gives high yields of monomeric cyanogen fluoride, b.p. -46° , which has been isolated in high purity by low-

gen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 99; (h) R. N. Haszeldine and A. G. Sharpe, "Fluorine and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 35; (i) A. A. Woolf, *J. Chem. Soc.*, 4121 (1953).