Table 1. Multiple-Pass Membrane Concentrator
(Feed concentration, UO_2^{++} = 0.01 molar)

RUNS	Flow Rate Ml./hr. Feed	Flow Rate Ml./hr. Strip.	UO_2^{++} Conc. Molar Raf. $\times 10^3$	UO_2^{++} Conc. Molar Ext.	H^+ Conc. Molar Raf. $\times 10^2$	H^+ Conc. Molar Ext.	EXT./STR.	α	θ	UO_2^{++} Flux $\times 10^5$ Moles/sq. in., hr.	Osmosis $\times 10^3$ Moles/sq. in., hr.
				Stripping concentration, H^+ = 2.0 molar							
4	3810	72.5	0.78	0.204	2.78	0.145	2.50	1.90	0.0	1.68	2.74
13	1654	22.8	0.75	0.262	2.56	0.071	2.48	1.38	1.0	1.85	2.34
14	1699	25.1	0.45	0.292	2.61	0.104	2.26	1.48	2.0	2.07	2.19
17	1646	24.7	0.38	0.300	2.60	0.135	2.25	1.50	3.0	2.09	2.15
				Stripping concentration, H^+ = 3.0 molar							
29	1698	18.4	0.437	0.2440	2.55	0.121	3.64	1.62	0.0	2.04	3.37
25	1678	15.8	0.455	0.3093	2.71	0.057	3.31	1.41	1.0	2.02	2.54
24	1669	16.3	0.397	0.3168	2.71	0.088	3.18	1.47	2.0	2.05	2.47
35	1681	16.1	0.387	0.3180	2.69	0.096	3.14	1.44	3.0	2.01	2.40

$\frac{\text{EXT.}}{\text{STR.}}$ = volumetric ratio of extract to strip streams

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NOTATION

a = activity
C = concentration
E_{Don} = Donnan potential
F = Faraday's constant
M = molar
R = gas constant
T = absolute temperature
Z = valence
α = ratio of equivalents of ions in strip stream to equivalents of ions in feed stream valents of ions in feed stream
θ = recycle ratio; ratio of volumetric flow rate of recycling extract to volumetric flow rate of make-up stripping acid.

Subscripts

l = left side
r = right side

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Separation of Shape and Polarity Effects for Polar Fluids

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In recent papers, Halm and Stiel have defined a fourth parameter for polar fluids through the vapor pressure and have shown that this approach is applicable for the entropy of vaporization (*1*), density of saturated liquids and vapors (*2*), and second virial coefficients (*3*). This method has been successfully applied also for other properties, including the heat capacity of saturated liquids (*4*), and surface tension of polar fluids (*5*). In the definitions of the shape and polarity parameters ω and x, the effects of the different types of molecular interaction are not separated, so that although the parameters have considerable utility, they do not each have direct physical significance.

The reduced vapor pressure of a polar fluid can be expressed as

$$P_R = f\left(T_R, \frac{a}{\rho_0}, \frac{\mu^2}{\epsilon \rho_0{}^3}\right) \qquad (1)$$

where a/ρ_0 is the shape group and $\mu^2/\epsilon\rho_0{}^3$ the polarity group for a four-parameter intermolecular potential function, such as the Kihara spherical core potential with an added term for dipole-dipole interactions. For normal (nonpolar and slightly polar) fluids Pitzer (4) defined a macroscopic shape parameter ω as

$$\omega = -1.000 - \log P_R|_{T_R=0.7} \qquad (2)$$

For polar fluids, Halm and Stiel retained Equation (2) so that ω for a polar fluid includes both shape and polarity effects, and the fourth parameter was defined as

$$x = \log P_R|_{T_R=0.6} - \log P_{Rn}|_{T_R=0.6}$$

$$= \log P_R|_{T_R=0.6} + 1.70\omega + 1.552 \qquad (3)$$

In this study, alternate parameters ω' and x' have been considered, which are related to ω and x as follows:

$$\omega = \omega' + x' \qquad (4)$$

$$x = 0.14x' - 1.1\omega'x' \qquad (5)$$

where ω' and $x' \geqq 0$. Equations (4) and (5) result from an expansion of $\log P_R$ in ω' and x' at $T_R = 0.7$ and $T_R = 0.6$, respectively. Equation (4) is the simplest relationship which can be postulated which allows for some separation of ω into shape and polarity contributions. A previous attempt at the separation of ω into shape and polarity contributions has been provided by Thompson and Braun (6). The value of 0.14 in Equation (5) was determined from ω and x for hydrogen chloride, for which substance $\omega' \simeq 0$ (and therefore $\omega \simeq x'$). The coefficient of $\omega'x'$ in Equation (5) was determined by trial and error to insure that the values of ω' and x' were positive for all the fluids considered, including substances with negative values of x such as *n*-butanol.

Values of ω and x and of ω' and x' for a number of polar fluids are included in Table 1. It can be seen that the parameters ω' and x' are more physically realistic; the values of ω' follow a reasonable trend with the actual size of the molecule. This aspect helps in detecting erroneous parameters resulting from poor vapor pressure data. Although Equations (4) and (5) are still simple approximations for the actual dependence of the reduced vapor pressure on shape and polarity variables, it is felt that the parameters ω' and x' follow essentially the same trend as actual molecular groups. Any discrepancies for individual substances can be due to errors in the available critical constants for the substance or in the vapor pressure data used to establish ω and x.

An interesting result can be obtained by the rearrangement of Equation (5) as

$$x = x'(0.14 - 1.1\omega') \qquad (6)$$

Since $x' \geqq 0$, Equation (6) predicts that x should be positive for $\omega' < 0.13$ and negative for larger values of the shape factor. Negative values of x are obtained for alcohols of larger molecular size than ethyl alcohol, for which substance $\omega' \simeq 0.13$. Thus, the $\omega'x'$ term in Equation (5) is necessary to provide physically-significant parameters and evidently accounts for the effect of dipole-induced dipole interactions.

TABLE 1. VALUES OF ω AND x AND ω' AND x' FOR POLAR FLUIDS

Substance	ω	x	ω'	x'
Water	0.344	0.023	0.055	0.289
Hydrogen chloride	0.125	0.016	0.017	0.108
Methanol	0.556	0.037	0.060	0.496
Ethanol	0.639	0.003	0.122	0.517
n-Propanol	0.626	−0.057	0.275	0.351
iso-Propanol	0.663	−0.053	0.242	0.421
n-Butanol	0.59	−0.07	0.35	0.24
Ethyl ether	0.275	−0.003	0.149	0.126
Ammonia	0.252	0.013	0.064	0.188
Methyl chloride	0.152	0.007	0.058	0.092
Ethyl chloride	0.191	0.005	0.085	0.106
Methyl fluoride	0.191	0.012	0.050	0.141
Acetone	0.304	0.013	0.076	0.228
Ethyl mercaptan	0.186	0.004	0.090	0.096
Ethylene oxide	0.207	0.013	0.055	0.152

Although the parameters ω' and x' provide additional insight into the fourth parameter approach, these quantities are not necessarily more useful than the original parameters ω and x. For example, for the critical compressibility factor of polar fluids, Halm and Stiel (2) obtained the relationship

$$Z_c = 0.291 - 0.114\omega - 1.42x + 0.069\omega^2 - 7.05x^2 + 1.51\omega x \qquad (7)$$

If Equations (4) and (5) are substituted into Equation (7), cubic terms in ω' and x' would result. For a substance such as ethyl alcohol, the $\omega'(x')^2$ term is as large as the $\omega'x'$ term for other fluids. Thus, a cubic expansion of a reduced property in ω' and x' would be required in order to obtain accuracy comparable to that for the quadratic expansion in ω and x.

The use of linear definitions for the shape and polarity parameters has considerable pragmatic advantage in that it enables other properties of a polar fluid to be related to the vapor pressure and reduces the deviations of a property from the values calculated from the normal fluid relationship.

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NOTATION

a = radius of spherical core
P_R = reduced vapor pressure
T_R = reduced temperature
x = fourth parameter defined in Equation (3)
x' = fourth parameter defined in Equations (4) and (5)
Z_c = critical compressibility factor

Greek Letters

ϵ = energy parameter of intermolecular potential function
μ = dipole moment of molecule, debyes
ρ_0 = distance parameter of intermolecular potential function
ω = acentric factor
ω' = third parameter defined in Equations (4) and (5)

Subscript

n = normal fluid

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