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Properties of Organic–Water Mixtures

Activity Coefficients of Sodium Chloride at Saturation in Aqueous Solutions of Some Oxy-Oxa Compounds at 25° C

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The solubility of NaCl in aqueous solutions of a number of organic solvents was determined at 25° C by packed column techniques. The solvents were primarily low-molecular-weight diols, cellosolves, or carbitols. From the solubility data, activity coefficients $\gamma_\pm^*$ of NaCl can be computed. For solutions containing 5% water, log $\gamma_\pm^*$, as a first approximation, varies linearly with the number of carbon atoms in a given series.

As part of the continuing study of water desalination by hyperfiltration (separation of salts from water by filtration through suitable membranes under pressure), thermodynamic and transport data for a variety of organic–water mixtures have been collected. Previous papers (*1, 3*) dealt with the comparison of activity coefficients of several salts, including NaCl, in aqueous organic solutions at saturation. The present paper summarizes a large number of solubility measurements at 25° C for NaCl in 21 different organic compounds as a function of water content. The compounds are primarily low-molecular-weight diols, cellosolves, or carbitols. They can be classified under the types R″OR′OH or R″OR′OROH where R and R′ range from $-C_2H_4-$ to $-C_6H_{12}-$, and R″ ranges from —H to $-C_4H_9$.

EXPERIMENTAL

Packed Column Method. The packed column technique for measuring solubilities has been described previously (*3*). It involves passage of a solution through a small column filled with salt plus analysis of the effluent. Columns of 0.6-cm diameter were filled to a height of 6 to 8 cm with fine grained (ca. 50 mesh) NaCl; gravity flow rates were ca. 1 cm/min which, according to earlier studies, and confirmed in occasional cross-checks here, were easily within the range demanded by the 0.1% analytical precision and corresponding approach to equilibrium.

The effluent samples were weighed and analyzed. The salt concentration was established by chloride titration with silver nitrate, using chromate as indicator.

Materials. *Salt.* Reagent grade NaCl was used, with a stated maximum impurity of 0.025%. It was dried at 400° C for 24 hr to remove traces of moisture.

Organic Compounds. All of the compounds used were commercial materials that were further purified by crystallization, distribution, and fractional distillation where appropriate. The middle portions from the distillation step (bp range < 1°) were reserved for this study. They were checked to be essentially water-free. Mixtures with water were prepared by weight to give generally five different water contents, 5, 15, 25, 50, and 75%.

RESULTS AND DISCUSSION

Solubility Measurements. The solubility of NaCl was measured at 25° C in aqueous solutions of 21 different organic compounds. The results are given in Table I in terms of grams of NaCl dissolved in 1 kg of mixed solvent. In most cases, measurements were made over the entire range of organic–water composition. For a few compounds, however, limited miscibility in the presence of NaCl determined the range of composition studied. Water-free measurements could not be made in three of the compounds that are solids at 25° C: but-2-yne-1,4-diol, 2,2-dimethylpropane-1,3-diol, and 2-methyl-2-ethylpropane-1,3-diol.

Table I. Solubility of NaCl in Organic–Water Mixtures at 25° C

No.	Compound	Wt % organic	Solubility, g/kg solvent	$\gamma_{\pm}^{*}$
1	Butane-1,3-diol, $CH_3CH(OH)C_2H_4OH$	25.51	222.0	1.21
		50.09	113.1	1.60
		75.04	32.6	2.77
		85.01	14.1	3.84
		95.02	4.82	3.74
		100.0	2.73	
2	Butane-1,4-diol, $CH_2(OH)C_3H_6OH$	24.99	231	1.18
		50.01	119.8	1.51
		74.96	33.9	2.67
		84.89	15.0	3.65
		94.82	5.04	3.72
		100.0	2.69	
3	But-2-ene-1,4-diol, $CH_2(OH)CH{=}CHCH_2OH$	25.00	238.8	1.14
		50.00	132.8	1.36
		75.00	47.2	1.92
		85.00	23.7	2.29
		94.98	9.91	1.83
		100.0	6.02	
4	2-Butoxyethane-1-ol (butyl cellosolve), $C_4H_9OC_2H_4OH$	30.39	[a]	
		60.36	[a]	
		90.05	9.42	3.82
		91.99	6.01	4.82
		94.06	3.36	6.40
		95.92	1.73	8.58
		97.95	0.76	9.76
		100.0	0.29	
5	2-Butoxy,1-(2′-hydroxypropoxy)ethane, $C_4H_9OC_2H_4OC_3H_6OH$	75.01	[a]	
		84.99	[a]	
		95.06	0.835	21.4
		100.0	0.067	
6	But-2-yne-1,4-diol, $CH_2(OH)C{\equiv}CCH_2OH$	25.00	244.5	1.11
		49.99	143.7	1.26
		77.51	59.5	1.49
		100.0	[b]	
7	2,2-Dimethylpropane-1,3-diol, $CH_2(OH)C(CH_3)_2CH_2OH$	25.10	228.3	1.19
		49.94	129.3	1.40
		75.02	42.4	2.13
		85.82	18.6	2.76
		100.0	[b]	
8	2-Ethoxyethane-1-ol (cellosolve), $C_2H_5OC_2H_4OH$	25.10	219.9	1.23
		50.60	116.4	1.54
		75.08	38.0	2.37
		85.23	16.6	3.21
		95.03	4.39	4.10
		100.0	1.24	
9	2-Ethoxy,1-(2′-hydroxyethoxy)ethane (carbitol), $C_2H_5OC_2H_4OC_2H_4OH$	24.98	227.6	1.19
		50.01	118.9	1.52
		75.01	38.0	2.38
		84.86	17.2	3.19
		94.97	4.62	3.94
		100.0	1.33	
10	Hexane-2,5-diol, $CH_3CH(OH)C_2H_4CH(OH)CH_3$	25.01	222.0	1.22
		50.04	117.8	1.54
		75.02	29.2	3.10
		85.00	7.65	7.10
		94.97	0.70	26.0
		100.0	0.12	
11	2-Methoxyethane-1-ol, $CH_3OC_2H_4OH$	25.10	229.2	1.18
		50.63	125.6	1.42
		75.08	51.8	1.74
		85.34	30.6	1.73
		95.03	15.2	1.18
		100.0	8.41	
12	2-Methoxy,1-(2′-hydroxyethoxy)ethane, (methyl carbitol), $CH_3OC_2H_4OC_2H_4OH$	24.98	233.5	1.16
		50.02	129.2	1.40
		75.00	49.6	1.82
		84.89	27.1	2.02
		95.16	10.1	1.74
		100.0	4.04	
13	2-Methoxypropane-1-ol, $CH_3OC_3H_6OH$	25.00	222.0	1.22
		50.01	120.1	1.51
		74.98	36.3	2.50
		84.98	14.9	3.65
		95.07	2.56	6.97
		100.0	0.05	
14	2-Methoxy,1-(2′-hydroxypropoxy)propane, $CH_3OC_3H_6OC_3H_6OH$	25.00	226.2	1.20
		49.91	123.4	1.47
		75.04	39.7	2.28
		85.06	16.8	3.22
		95.04	3.85	4.67
		100.0	1.09	
15	2-Methyl-2-ethylpropane-1,3-diol, $CH_2(OH)C(CH_3)(C_2H_5)CH_2OH$	49.93	[a]	
		75.06	[a]	
		85.00	27.2	2.00
		90.04	12.2	2.96
		100.0	[b]	
16	2-Methylpentane-2,4-diol, $CH_3CH(OH)CH_2C(CH_3)$-$(OH)CH_3$	50.01	[a]	
		74.97	[a]	
		90.00	3.78	9.58
		95.01	1.00	18.1
		100.0	0.23	
17	Bis(2-hydroxyethyl)ether, $CH_2(OH)CH_2OC_2H_4OH$	24.79	253.1	1.08
		50.07	160.6	1.12
		75.04	88.4	1.02
		84.89	68.8	0.79
		95.09	51.9	0.34
		100.0	45.4	
18	Bis(1-methyl-2-hydroxyethyl)ether, $CH_2(OH)CH(CH_3)OCH(CH_3)CH_2OH$	25.45	229.1	1.18
		50.10	127.3	1.42
		75.06	48.8	1.85
		85.05	27.4	1.97
		95.04	12.3	1.46
		100.0	6.09	
19	Pentane-1,5-diol, $CH_2(OH)C_4H_8OH$	25.10	230.2	1.18
		50.30	121.7	1.48
		74.92	34.7	2.62
		85.06	12.0	4.51
		94.84	2.68	6.97
		100.0	1.02	
20	Propane-1,2-diol, $CH_3CH(OH)CH_2OH$	25.06	237.3	1.14
		50.13	141.7	1.27
		75.03	68.8	1.31
		85.08	48.7	1.11
		95.02	34.4	0.52
		100.0	28.8	
21	Propane-1,3-diol, $CH_2(OH)C_2H_4OH$	25.00	224.2	1.21
		49.94	122.3	1.48
		74.85	47.6	1.91
		85.00	26.8	2.03
		94.99	14.9	1.22
		100.0	11.3	

[a] Immiscible mixture when saturated with NaCl. [b] Solid at 25° C.

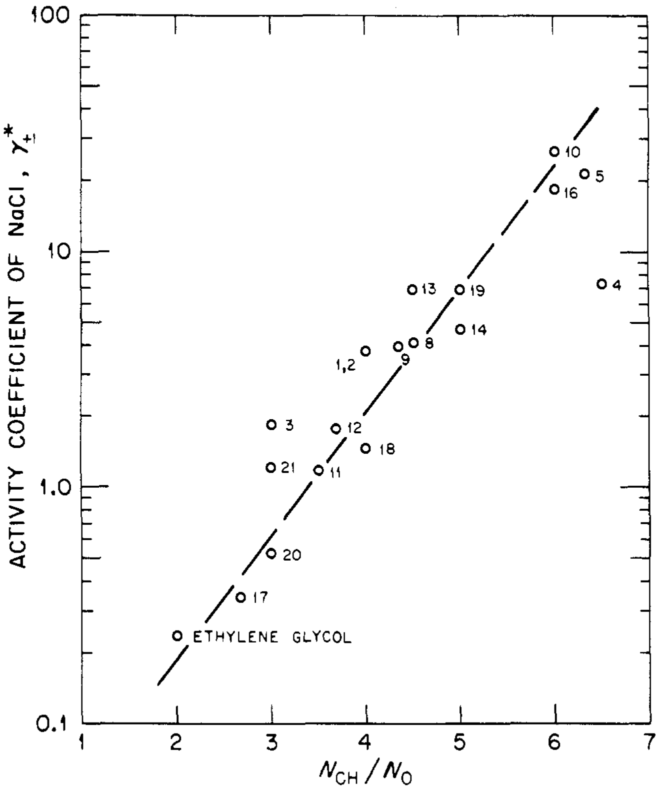

Figure 1. Activity coefficients of sodium chloride at saturation in solutions of some oxy-oxa compounds containing 5% water

N_{CH} = no. of carbon—hydrogen bonds, N_O = no. of oxygen atoms, compounds identified in Table I

The solubility of NaCl in 5% water mixtures of 2-methoxyethane-1-ol and 2-methoxy,1-(2′-hydroxyethoxy)ethane can be compared with previous results at 50° C (*1*). In both cases the solubilities are about 25% higher at 25° C.

For the straight-chain compounds, the solubility of NaCl at a given water content decreases as mol wt increases, as had been previously observed with glycols (*1*), glycol monomethyl ethers (*1*), and alcohols (*4*). Branching has a measurable effect on solubility but, as might be expected, the effect becomes less pronounced as the chain length increases. For example, at water contents less than 15%, the solubilities of NaCl in the propane diols differ by a factor of two or more; for the butane diols, the solubilities are nearly the same over the entire composition range. Comparison of the results for the 5-carbon diols (pentane-1,5-diol and 2,2-dimethylpropane-1,3-diol) shows that branching not involving functional groups can also result in a higher NaCl solubility at low water contents.

The effect of unsaturation on the solubility of NaCl can be seen for the 4-carbon diols. The solubility at any water content increases as the unsaturation increases, being highest in water mixtures of but-2-yne-1,4-diol.

It is interesting to note that in two pairs of isomers involving a diol and a monoether, the solubility of NaCl is nearly the same in each at any given water content—i.e., for propane-1,3-diol and 2-methoxyethane-1-ol and for butane-1,4-diol and 2-ethoxyethane-1-ol.

Activity Coefficients of NaCl. The results for the different compounds can also be compared in terms of an activity coefficient $\gamma^*_\pm$, which is computed on the same basis as that in water ($\gamma_\pm$), namely, by using the same standard state as in water and expressing concentrations in mol/kg of water. The $\gamma^*_\pm$ is a measure of the relative selectivity of the medium for salt and water; it is a useful quantity for evaluation of model solutions for hyperfiltration membranes (*1, 2*).

If s_{aq} is the solubility in pure water and s_o is the solubility in the water-organic mixture, both expressed in mol/kg of solvent, and f_w is the fractional water content of the solvent (kg of H_2O/kg of solvent), $\gamma^*_\pm$ is given by (*3*):

$$\gamma^*_\pm = s_{aq} f_w \gamma_\pm / s_o$$

The solubility of NaCl in pure water, s_{aq}, was taken to be 360 g/kg of H_2O at 25° C (*4*), and $\gamma_\pm$ = 1.006 (*3*).

The values of $\gamma^*_\pm$ in 5% water mixtures are shown in Figure 1 as a function of N_{CH}/N_O where N_{CH} is the number of carbon—hydrogen bonds and N_O is the number of oxygen atoms present in the molecule. The value for ethylene glycol (*3*) is also included. The logarithm of the activity coefficients for these two series (R″OROH and R″OR′OROH) increases roughly linearly with this ratio. The equation for the dashed line in Figure 1 is

$$\log \gamma^*_\pm = -1.8 + 0.53\, N_{CH}/N_O$$

Activity coefficients in some of the higher members of the polymer series of polyethylene glycols and their monomethyl ethers (*1*) also fall near this straight line. The activity coefficients in the dimethyl ethers and the highest molecular-weight members of the other two polymer series, however, are far above those predicted from Figure 1. Thus, although the relationship could be used to approximate activity coefficients for other members of the series studied here, it should not be used for widely differing series.

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NOMENCLATURE

f_w = wt fraction H_2O in water-organic mixture
N_{CH} = number of hydrogen atoms attached to carbon atoms in molecule (C—H bonds)
N_O = number of oxygen atoms in molecule
s_{aq} = solubility of NaCl in water (mol/kg water)
s_o = solubility of NaCl in water-organic mixture (mol/kg solvent)
$\gamma_\pm$ = mean activity coefficient of NaCl in water
$\gamma^*_\pm$ = mean activity coefficient of NaCl in water-organic mixture (for concentrations expressed as mol/kg water)

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