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Influence of Temperature on the Liquid–Liquid Equilibrium of the Water–*n*-Butyl Alcohol–Sodium Chloride System

R. De Santis,[†] L. Marrelli,* and P. N. Muscetta[‡]
Cattedra di Principi di Ingegneria Chimica, Facoltà di Ingegneria dell'Università di Roma, Italy

Experimental data are reported for the liquid–liquid equilibrium of the water–n-butyl alcohol–sodium chloride system in the range 20–40 °C. The observed Setschenow constants are compared with the results of the scaled-particle theory.

In a previous work (*4*) a thorough research was carried out on the liquid–liquid equilibria of ternary systems, water–sodium chloride–saturated aliphatic alcohol with three or four carbon atoms, at a temperature of 25 °C. The aim of the analysis was to characterize the thermodynamic behavior of these systems which have been extensively studied with respect to vapor–liquid equilibrium. In addition the interpretation of experimental results showed *n*-butyl alcohol (NBA) to be the most suitable of the series examined for sea water desalination by solvent extraction (*2, 4, 13*). However, NBA is inferior in selectivity to certain secondary and tertiary amines (*3*). The importance of the H_2O–NBA–NaCl system requires a more complete characterization of the temperature dependence of the salting-out effect. The only experimental results in literature seem to be those obtained by Reber et al. (*17*), concerning the NaCl effect on the mutual solubility of NBA and H_2O in the salt concentration range 0.02–0.08 (mole fractions) and for temperatures between 90 °C and the critical solubility temperature of the water–alcohol binary system.

Comparison of the observed Setschenow (*19*) constants with the values estimated by the scaled particle theory (*10, 14, 15, 20*) is also a matter of great interest.

Experimental Section

The measurements of the solubility limits have been carried out at 20, 30, and 40 °C using separator funnels with a thermostatic jacket for temperature control (±0.1 °C). Extractors were loaded with equal quantities of NBA and NaCl solution at concentrations between zero and the saturation value in the water. Experiments at 20 °C were carried out with three ratios (1, 1/3, 3 wt) of aqueous salt solution/alcohol. After an extended period of mixing and a quantitative gravity separation, samples were withdrawn from both phases. Equilibrium compositions were determined by analyzing the alcohol in the aqueous phase and the salt in both phases. Water and alcohol concentrations in the organic phase were derived from a material balance based upon the initial quantities and compositions.

The sodium chloride determinations were carried out with a Philips conductivitymeter. Alcohol in the aqueous phase was determined by colorimetric analysis (double beam Lange colorimeter) of the cerium complex, as proposed by Reid and Salmon (*18*). Each of the determinations was carried out with several repetitions. The standard deviations were derived and yielded reproducibilities in each case of 0.005 as weight fractions.

The alcohol used in the tests was obtained from Carlo Erba with analytical purity and was refractionated before use. Sodium chloride, RP purity, was obtained from Carlo Erba; dissolution water was prepared by a double distillation.

The experimental results on weight compositions of organic and aqueous phases for the different temperatures are shown in Tables I–III.

Discussion

The measurements of the solubility limits for the water–alcohol binary system at 20, 30, and 40 °C, and those at 25 °C (*4*), have been compared with data reported by other authors (*1, 5, 6, 8*). Figure 1 shows a good agreement between our observations and those reported in the literature.

The salt effect on the mutual water–alcohol solubility is shown in Figure 2. It is observed that salt induces a gradual miscibility gap which increases in width with the salt concentration.

Temperature effects, in the analyzed range, are similar to those observed for the binary system.

Temperature and salt concentration affect also the salt distribution between the two phases.

It can be observed (Figure 3), in this case, that the temperature effect is very small but such as to determine, as temperature increases, higher salt concentrations in the organic phase.

Salt concentration in the aqueous phase, instead, yields an increase of salt content in the organic phase. This effect becomes gradually smaller as salt concentration in the aqueous phase increases.

In addition Figure 4 represents the NBA distribution curves which show alcohol concentration in the organic phase increasing as temperature decreases.

Davison et al. (*3*) found that, with tertiary and secondary amines, the solvent free selectivity was a function only of the mole fraction of water in the solvent phase, being approximately

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[†] Istituto di Chimica Applicata e Metallurgia, Facoltà di Ingegneria dell'Università di Cagliari.

[‡] Società Italiana Resine, Milano.

Table I. Liquid–Liquid Equilibrium of the System H_2O–n-C_4H_9OH–NaCl at 20 °C

$\beta^a = 1/3$				$\beta^a = 1$				$\beta^a = 3$			
O^b (wt %)		A^c (wt %)		O^b (wt %)		A^c (wt %)		O^b (wt %)		A^c (wt %)	
NBA	NaCl	NBA	NaCl	NBA	NaCl	NBA	NaCl	NBA	NaCl	NBA	NaCl
80.0	—	7.80	—	80.0	—	7.80	—	80.0	—	7.80	—
81.7	0.048	6.65	2.30	81.5	0.024	7.20	1.14	81.9	0.016	7.00	0.974
83.0	0.070	6.00	3.93	82.8	0.045	6.29	2.24	83.0	0.039	6.30	1.94
84.2	0.090	5.40	5.65	83.9	0.061	6.00	3.31	83.1	0.058	6.20	2.91
85.2	0.102	5.10	7.00	84.6	0.074	5.50	4.36	84.6	0.072	5.50	3.86
86.0	0.108	4.25	8.30	85.6	0.085	4.90	5.39	85.9	0.090	4.74	5.75
86.8	0.113	4.15	9.51	86.0	0.094	4.75	6.40	86.4	0.101	4.14	7.60
88.1	0.130	3.30	11.70	87.1	0.109	3.89	8.39	87.5	0.118	3.59	9.41
89.1	0.135	2.95	13.78	88.1	0.121	3.70	10.3	88.4	0.127	3.35	11.2
90.0	0.144	2.11	15.70	88.9	0.129	2.90	12.1	88.9	0.132	2.95	12.9
90.7	0.150	2.00	17.55	89.7	0.136	2.48	13.9	88.9	0.140	2.60	14.7
91.3	0.155	1.65	19.41	90.4	0.142	2.22	15.7	90.0	0.142	2.00	16.3
91.6	0.160	1.40	21.15	91.4	0.147	1.82	17.3	90.4	0.148	1.90	17.9
92.1	0.163	1.20	22.95	91.9	0.151	1.59	18.9	91.4	0.152	1.50	19.5
92.5	0.164	0.98	24.5	92.6	0.155	1.39	20.5	91.5	0.156	1.45	21.1
93.0[d]	0.165	0.91	25.8	93.1	0.158	1.21	22.0	92.4	0.159	1.10	22.6
93.4[d]	0.165	0.91	25.8	93.4	0.160	1.08	23.6	92.8	0.163	0.90	24.1
93.4[d]	0.165	0.91	25.8	93.6	0.163	0.95	25.0	92.2[d]	0.164	0.94	25.6
				94.0[d]	0.165	0.91	25.8	93.1[d]	0.165	0.91	25.8
				94.0[d]	0.165	0.91	25.8				

[a] β, aqueous salt solution wt/solvent wt. [b] O, organic phase. [c] A, aqueous phase. [d] At saturation.

Table II. Liquid–Liquid Equilibrium of the System H_2O–n-C_4H_9OH–NaCl at 30 °C

Organic phase (wt %)		Aqueous phase (wt %)	
NBA	NaCl	NBA	NaCl
79.4	—	7.10	—
81.2	0.026	6.42	1.15
82.2	0.045	5.70	2.26
83.2	0.061	5.44	3.34
84.0	0.075	5.00	4.41
84.6	0.086	4.59	5.45
85.2	0.096	4.24	6.48
86.2	0.111	3.60	8.50
87.2	0.123	3.04	10.5
88.0	0.132	2.59	12.4
88.6	0.140	2.45	14.2
89.7	0.146	1.81	16.0
90.5	0.150	1.51	17.7
91.1	0.155	1.23	19.1
92.0	0.158	1.03	21.0
92.4	0.161	0.89	22.6
92.9	0.164	0.75	24.1
93.2	0.166	0.69	25.5
93.4[a]	0.169	0.66	26.0

[a] At saturation.

Table III. Liquid–Liquid Equilibrium of the System H_2O–n-C_4H_9OH–NaCl at 40 °C

Organic phase (wt %)		Aqueous phase (wt %)	
NBA	NaCl	NBA	NaCl
78.6	—	6.60	—
80.3	0.021	5.96	1.19
81.6	0.041	5.25	2.31
82.4	0.060	4.70	3.42
83.1	0.072	4.61	4.53
83.6	0.085	4.21	5.58
84.4	0.095	3.86	6.65
85.4	0.111	3.27	8.69
86.3	0.122	2.78	10.6
87.1	0.131	2.31	12.5
87.9	0.139	1.90	14.4
88.6	0.146	1.70	16.2
89.5	0.151	1.28	17.8
90.4	0.156	1.01	19.4
91.0	0.160	0.82	21.0
91.5	0.163	0.66	22.6
92.0	0.166	0.54	24.1
92.3	0.170	0.50	25.6
92.8[a]	0.173	0.48	26.1
92.8[a]	0.173	0.48	26.1

[a] At saturation.

independent of salt and temperature except as these affected solvent-phase water content.

Plotting the selectivity, a straight line vs. mole percent water in the solvent phase was obtained passing through the critical solution composition at a selectivity of one.

From our data it appears this system may obey the same relation but with the selectivity lower than for the amines.

Prediction of the Setschenow Constant by the Scaled Particle Theory. The solubility of a nonelectrolyte in aqueous salt solutions can be expressed, as a first approximation, by the Setschenow empirical equation (*19*):

$$\log x_0/x = k_s C_s \tag{1}$$

where x_0 and x are the mole fractions of the nonelectrolyte in pure water and in the saline solution with salt molarity equal to C_s; the coefficient k_s depends only on the solvent–electrolyte pair and on temperature.

Since eq 1 is generally valid for very low saline concentrations, the correct definition of k_s is:

$$k_s = \left[\frac{\mathrm{d}\log (x_0/x)}{\mathrm{d}C_s}\right]_{C_s=0} \tag{2}$$

However, the Setschenow equation correlates the experimental results for the H_2O–NBA–NaCl system with good approximation in a large range of salt concentrations for the different temperatures examined.

Consequently the k_s value can be determined from all the data available and not only from those at low concentration. It is,

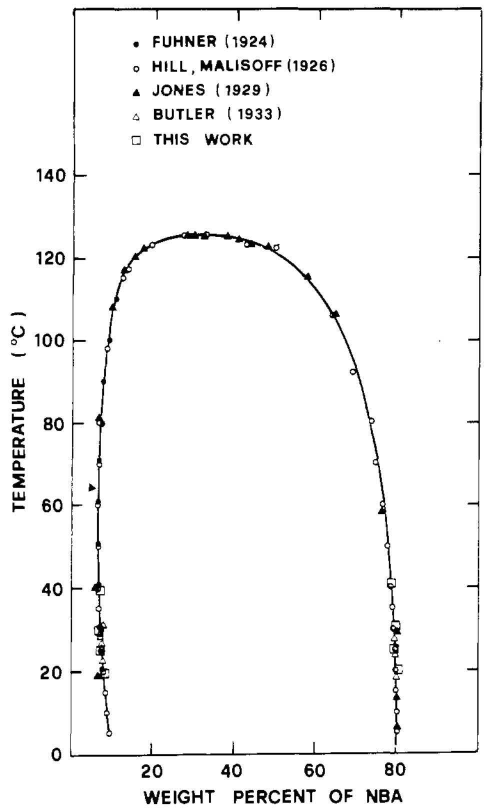

Figure 1. Miscibility gap of the water–*n*-butyl alcohol system.

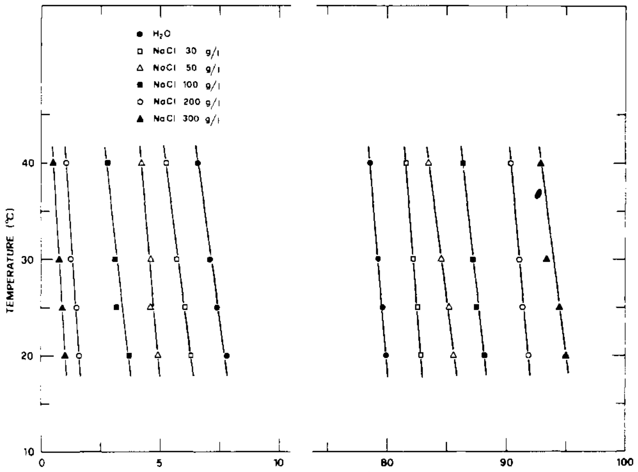

Figure 2. Influence of the salt concentration on the miscibility gap of the H_2O-NBA system.

therefore, more reliable. The experimental values are reported in Table IV for different temperatures. A small effect of temperature can be noticed.

As mentioned above, the salting constant k_s can be evaluated by using the scaled particle theory (*10, 14, 15, 20*), with satisfying results.

Extensions of the theory have been derived for nonpolar compounds. However, Wilcox and Schrier (*21*) have recently applied this method to aqueous systems containing polar nonelectrolytes such as saturated aliphatic alcohols.

The latter authors determined the experimental k_s of methanol, ethanol, and 1-propanol, in addition to that of ethylene glycol, by electrochemical methods. In fact the aqueous solutions of these alcohols do not show any miscibility gap at low salt concentrations. NBA is the first alcohol of the aliphatic series with a miscibility gap with pure water.

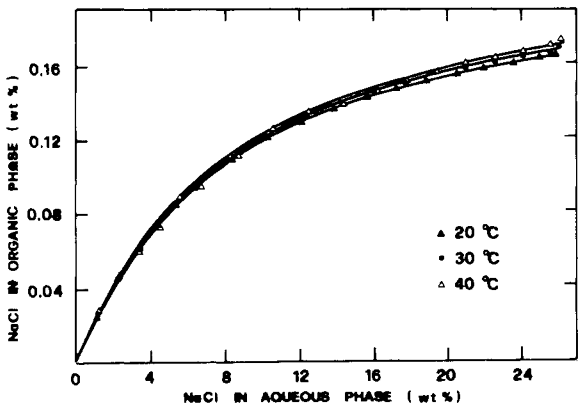

Figure 3. Distribution curves of NaCl in the organic and aqueous phase.

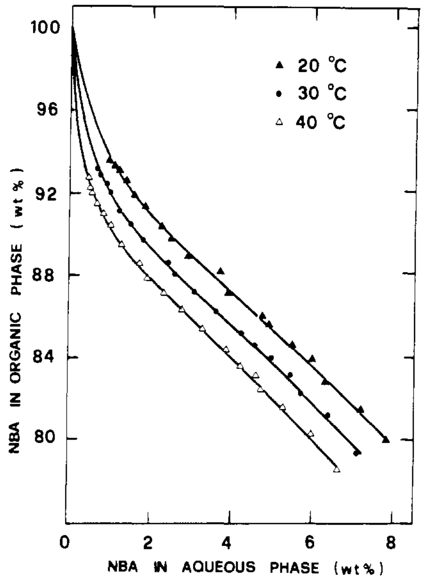

Figure 4. Distribution curves of NBA in the organic and aqueous phase.

The purpose of this work is not, therefore, a trivial extension of the Wilcox and Schrier procedure, the main difference being in the determination of k_s obtained from liquid–liquid equilibrium data and in the evaluation of the temperature influence on the Setschenow constant.

The procedure to evaluate k_s by the scaled-particle theory is based on the calculation of three contributions (*10*) to the salting constant k_s:

$$k_s = k_\alpha + k_\beta + k_\gamma \tag{3}$$

where k_α, positive in all cases, is linked to the salting-out and k_β, negative, characterizes the salting-in; k_γ is, generally, a very small quantity in comparison with k_α and k_β.

The expressions, obtained by Masterton and Lee (*10*) to evaluate the three contributions, require the knowledge of some molecular parameters which characterize the nonelectrolyte and the salt. Previous papers (*10, 21*) have shown that the calculated k_s strongly depends on the values of molecular diameter σ and energy parameter ϵ/K of the nonelectrolyte.

The value of these parameters depends on the particular expression chosen to describe the intermolecular potential and on the kind of experimental data used to evaluate σ and ϵ/K (transport properties, second virial coefficient, etc.).

In the case of alcohols a sufficiently correct formulation for the intermolecular potential is the Stockmayer expression (*7*).

Table IV. Observed and Calculated Values of the Setschenow Constant

T (°C)	k_s(obsd)	k_s(calcd)
20	0.175 ± 0.003	0.176
25	0.179 ± 0.005	0.179
30	0.186 ± 0.005	0.182
40	0.191 ± 0.005	0.187

However, the values of σ and ϵ/K, obtained by such an expression, are very different if experimental data of second virial coefficients (*16*) or of transport properties (viscosity) (*7*) are used. Molecular diameters of nonelectrolytes obtained from viscosity data, generally, yield more acceptable results (*21*) in the k_s evaluation.

For NBA the σ value derived from these data is unavailable. Its value was, therefore, deduced by extrapolating similar data pertaining to the series methanol, ethanol, and 1-propanol. The resulting value is close to 5.1×10^{-8} cm.

With regard to the energy parameters, on the other hand, the best results were obtained by using, both for ions and nonelectrolyte, the Mavroyannis–Stephen expression (*11*), instead of the values deduced from the Stockmayer potential (*10, 21*). The value thus obtained for NBA is: $\epsilon/K = 224$ K.

The polarizability of NBA was predicted by a method based on the addition of bond contributions (*12*). This procedure yields satisfying results for alcohol molecules. The value obtained for NBA is 8.6×10^{-24} cm^3/mol. The molecular parameters of the salt, needed to evaluate k_s, are reported by Masterton and Lee. The calculated k_s values are reported in Table IV at the four temperatures considered.

The agreement of the theoretical values with the observations (Figure 5) is good, especially considering the uncertainties in evaluating the molecular parameters.

As a consequence, the k_s dependence on temperature, which can be derived by the scaled-particle theory, is verified as a first approximation.

For a small range of temperatures this theory yields:

$$k_s = a + b/T \qquad (4)$$

where a is a positive term, resulting from the sum of k_α and k_γ (eq 3); it can be assumed to be constant with temperature. The term b/T is the variable negative term corresponding to k_β.

An expression similar to eq 4 can also be obtained by a thermodynamic derivation (see Appendix).

Comparing eq 4 with eq 5A, one can conclude that the term b is proportional to the derivative, with respect to C_s, of the partial molar enthalpy of the alcohol in saline water at infinite dilution.

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The authors wish to express their sincere thanks to A. R. Giona for the stimulating encouragement.

Appendix

The empirical Setschenow equation can be theoretically justified under particular hypotheses (*9*). The theoretical derivation of this equation follows a path in which the following expression is shown to hold:

$$\log \frac{x_0}{x} = \log \frac{\gamma}{\gamma_0} = k_s C_s \qquad (1A)$$

where γ and γ_0 are the activity coefficients of the solvent in the saline solution and in water without salt.

The left two terms in eq 1A are only equal if the solvent activity is unchanged as the water content varies with the reduction of water activity by salt. For most highly nonideal systems this is nearly true over the range of concentrations in the solvent phase encountered here.

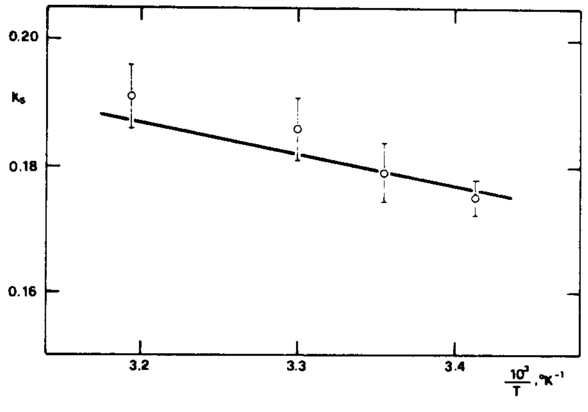

Figure 5. Calculated and experimental Setschenow constants.

From eq 2 and 1A it follows that:

$$k_s = \left[\frac{d \log (\gamma/\gamma_0)}{dC_s}\right]_{C_s=0} \qquad (2A)$$

The following dependence of k_s on temperature can be deduced from this equation:

$$\frac{dk_s}{dT} = \left[\frac{d}{dC_s}\frac{d \log (\gamma/\gamma_0)}{dT}\right]_{C_s=0} = \left[\frac{d(-\Delta H/RT^2)}{dC_s}\right]_{C_s=0} \qquad (3A)$$

where ΔH is the difference between the partial molar enthalpy of the nonelectrolyte in water and in the saline solution.

Equation 3A can be written as:

$$\frac{dk_s}{dT} = -\frac{A^\infty}{RT^2} \qquad (4A)$$

where A^∞ is the partial derivative, with respect to the salt concentration, of ΔH calculated at infinite salt dilution.

If A^∞ can be considered independent of temperature, or for small variations of the latter, eq 4A can be integrated to obtain an expression formally identical with that derived by the scaled particle theory:

$$k_s = \frac{A^\infty}{RT} + B \qquad (5A)$$

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