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Solubility of NaCl and KCl in Aqueous HCl from 20 to 85 °C

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The solubilities of NaCl and KCl in aqueous HCl solutions were determined from 20 to 85 °C at concentrations ranging from 0 to 20 g of HCl/100 g of solution. Equations are given that describe the solubilities over the range of conditions studied. For NaCl and KCl respectively measured solubilities show an average deviation from these equations of ±0.10 and ±0.08 g/100 g of saturated solution.

A complete understanding of the thermodynamics of concentrated aqueous electrolytes over a wide range of pressure, temperature, and composition requires data on the maximum concentrations of electrolytes that can be dissolved in aqueous media as a function of temperature. As a continuation of our investigations into the thermodynamics and phase equilibria of saturated aqueous electrolyte solutions at low (*1*) and elevated (*2*) temperatures, we have measured the solubilities of sodium and potassium chlorides in aqueous hydrochloric acid solutions from 20 to 85 °C. Before this study, published solubility data were confined to the interval 0-45 °C for both salts (*3*, *4*).

Experimental Method

The solubilities were determined by using the modified visual method of Potter and Clynne (*1*), except that the solvent was aqueous HCl of known concentration instead of water. The NaCl and KCl used were analytical reagent-grade salts, and the aqueous HCl solutions were prepared from analyzed reagent-grade aqueous HCl. Temperatures were measured by using platinum resistance thermometers calibrated against NBS secondary standards; all temperatures are accurate to ±0.05 °C and are on the IPTS-68 scale.

Results

The experimental solubilities determined for NaCl and KCl in aqueous HCl are tabulated in Tables I and II, respectively. Solubilities are reported as grams of anhydrous salt per 100 grams of solution (g/100 g), as a function of the concentration of anhydrous HCl in g/100 g and temperature in degrees Celsius. The data were regressed via a nonlinear least-squares program to an equation of the form

$$S = a_0 + a_1T + a_2T^2 + a_3\chi T + a_4\chi T^2 + a_5\chi^2 T + a_6\chi + a_7\chi^2$$

where S is the solubility of the salt in g/100 g, χ is the concentration of anhydrous HCl in g/100 g, T is the temperature in degrees Celsius (IPTS-68), and a_i are the regression coefficients. The regression coefficients for the equations describing NaCl and KCl solubility in aqueous HCl solutions are listed in Table III.

Table I. Experimental Solubility of NaCl in Aqueous HCl Solutions[a]

T, °C	amt of HCl	amt of NaCl
34.70	3.97	20.56
55.46	3.94	21.23
73.19	3.90	21.91
35.29	8.61	13.94
46.33	8.50	15.00
63.06	8.43	15.71
32.90	13.79	8.08
40.05	13.70	8.67
51.36	13.56	9.58
76.28	13.38	10.79
36.26	19.26	3.68
44.20	19.19	4.07
62.73	18.99	5.04
85.68	18.78	6.08

[a] Concentrations are in g/100 g.

Table II. Experimental Solubility of KCl in Aqueous HCl Solutions[a]

T, °C	amt of HCl	amt of KCl
24.86	4.02	19.61
58.75	3.75	24.97
68.64	3.68	26.45
82.39	3.59	28.10
23.89	8.70	12.97
39.51	8.46	15.43
65.80	8.03	19.68
74.19	7.89	21.08
87.23	7.72	22.84
24.88	13.88	7.49
53.92	13.24	11.71
62.60	13.05	13.02
70.02	12.88	14.16
25.93	19.21	3.93
40.96	18.94	5.29
58.46	18.49	7.54
87.19	17.75	11.24

[a] Concentrations are in g/100 g.

Table III. Regression Coefficients for Equations Describing Solubility of NaCl and KCl in Aqueous HCl Solutions[a]

	NaCl	KCl
a_0	26.076	22.055
a_1	1.207×10^{-2}	0.1793
a_2	6.1845×10^{-5}	-4.373×10^{-4}
a_3	6.7761×10^{-3}	-1.201×10^{-3}
a_4	-5.625×10^{-6}	3.3911×10^{-5}
a_5	-2.63197×10^{-4}	-2.18184×10^{-4}
a_6	−1.88997	1.7917
a_7	3.3468×10^{-2}	3.8223×10^{-2}
mean devn	±0.10	±0.08

[a] Temperatures are in IPTS-68 degrees Celsius, and concentrations are in g/100 g. Equations are valid from 20 to 85 °C for concentrations of HCl from 0 to 20 g/100 g.

Discussion

Data from older literature (*3*, 1886-1941) agree with the solubility equations determined in this study to within ±0.3 g/100 g for both KCl and NaCl. A more recent study by Volz-Fladrich (*4*), covering the range from 0 to 45 °C, agrees with the regression equations to within ±0.18 g/100 g for NaCl solubilities and ±0.13 g/100 g for KCl, within the experimental uncertainties of both data sets. However, in dilute HCl solutions, where Volz-Fladrich made only a limited number of determinations, the measured values are consistently higher than those determined by us. If the equations in Table III are extrapolated to a concentration of 0 g of HCl/100 g, the calculated values agree within experimental uncertainties with the data of Potter and Clynne (*1*) for the solubilities of NaCl and KCl in pure water.

Literature Cited

(1) Potter, R. W., II, Clynne, M. A., *J. Res. U.S. Geol. Surv.*, **6**, 701 (1978).
(2) Potter, R. W., II, Babcock, R. S., Brown, D. L., *J. Res. U.S. Geol. Surv.*, **5**, 389 (1977).
(3) Linke, W. F., "Solubilities of Inorganic and Metal Organic Compounds", 4th ed., Vol. 2, American Chemical Society, Washington, D.C., 1965.
(4) Volz-Fladrich, H., *Freiberg. Forschungsh. C*, **134**, 1 (1962).

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Equilibrium Phase Properties of the Toluene–Hydrogen Sulfide and *n*-Heptane–Hydrogen Sulfide Binary Systems

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Vapor and liquid equilibrium phase compositions have been determined for the toluene–hydrogen sulfide and *n*-heptane–hydrogen sulfide binary systems at temperatures of 100.0, 175.0, 250.0, and 400.0 °F at several pressures between the vapor pressure of the hydrocarbon component and the vapor pressure of hydrogen sulfide or the critical pressure for the system, whichever was higher. Refractive index measurements were made on the equilibrium vapor and liquid phases for the hydrogen sulfide–*n*-heptane system at the three lower temperatures. These measurements were used with the phase composition data to calculate the equilibrium phase densities using the Lorentz–Lorenz molar refractivity relationship.

Introduction

Hydrogen sulfide is frequently found in naturally occurring hydrocarbon reservoirs and it is one of the more common nonhydrocarbon components found in substitute fuel mixtures derived from heavy oils, bitumen, or coal. Thus any method used for calculating the properties or phase behavior of these complex mixtures must be capable of coping with the presence of hydrogen sulfide. Normally, calculation methods require a knowledge of the properties of the pure components in the system, and in the case of hydrocarbon–nonhydrocarbon mixtures, they require at least one characteristic parameter for each possible hydrocarbon–nonhydrocarbon binary pair that could be formed from the mixture. In cases where the individual hydrocarbon components in the higher molecular weight fractions are not identified, it is common practice to at least attempt to characterize the fraction according to its paraffinic, aromatic, naphthenic, and sometimes olefinic content. Thus the binary interactions between the nonhydrocarbons and the fractions must be estimated. In order to make good estimates of these parameters, it is essential to have at least some values based on experimental data for selected representatives of each group.

The object of the work presented in this paper was to obtain experimental data which would make it possible to calculate binary interaction parameters for hydrogen sulfide with *n*-heptane, a C_7 paraffin, and toluene the C_7 aromatic. The work represents a continuation of the studies on related systems which have recently been reported by Ng and Robinson (*10*, *11*) and Kalra et al. (*9*). No previous studies were found in the literature on the *n*-heptane–hydrogen sulfide system. The only previous work on the toluene–hydrogen sulfide system was that of Gerrard (*6*) on the solubility of hydrogen sulfide in toluene at a total pressure of 754 mmHg over a temperature range from −8 to +20 °C.

Experimental Method

The experimental methods used in this work were the same in all respects as those described by Kalra et al. (*9*) and by Ng and Robinson (*10*, *11*) for their work on carbon dioxide with toluene and *n*-heptane and carbon dioxide and hydrogen sulfide with methylcyclohexane. The variable volume equilibrium cell described in detail by Besserer and Robinson (*2*, *3*) was used for the studies on hydrogen sulfide and *n*-heptane at 100, 175, and 250 °F. Refractive index measurements were made on the equilibrium vapor and liquid phases at each temperature. The fixed volume cell described in detail by Ng and Robinson (*10*) was used for this system at 400 °F and also for all of the work on hydrogen sulfide and toluene. No refractive index measurements were made on the hydrogen sulfide–toluene system.

Samples of the vapor phase were obtained from the variable volume cell using the technique explained by Besserer and Robinson (*2*, *3*) and from the constant volume cell using a specially designed valve described by Kalra and Robinson (*8*). Samples of the liquid phase from the variable volume cell were obtained by trapping a sample of the equilibrium liquid in one chamber of a four-way ball valve and then vaporizing it into a stream of circulating hot helium. A similar sample of the liquid from the constant volume cell was obtained by using a device similar to that described by Fredenslund et al. (*5*). In all cases, the methods permitted the removal of microsamples so that the cell conditions were not materially altered during the sampling process.

Materials Used

The hydrogen sulfide used in these studies was obtained as a specially prepared sample from Thio-Pet Chemicals Limited, Fort Saskatchewan, Alberta, Canada. The liquid phase of this material was distilled once and the condensed phase from the distillation was used for the experiments. This minimized contamination with carbon dioxide and mercaptans. The purity of the material was at least 99.9 mol % as determined by chromatographic analysis. The toluene was research grade supplied by Phillips Petroleum Co. with a purity of 99.94 mol %. The *n*-heptane was supplied by Aldrich Chemicals at a stated purity of 99+ mol % but a chromatographic scan indicated it to be better than 99.9+ % pure. Both of these materials were used without further purification.

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