Solubility of Lithium Fluoride in Water

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The solubility of lithium fluoride in water increases only slightly with temperature in the range measured, going from 0.132% at 23.7°C to 0.150% at 81.8°C. The solubility product of lithium fluoride determined at 30°C in the presence of the common ions agreed within 0.2×10^{-3} of the 2.8×10^{-3} value calculated from flame photometric lithium measurements made at the same temperature on pure lithium fluoride solutions. Solubility results verify those determined gravimetrically over the range of 0–35°C by Payne in 1937.

Although some water solubility data for lithium fluoride is in the literature (*5*), the published values in the range of general interest, i.e., 0–100°C are sparse and somewhat erratic. The most consistent set of data is that of Payne (*4*) which covers the range of 0–35°C. The triple purpose of this work was to verify Payne's data, to extend measurement to higher temperatures, and to determine the effect of the common ion by calculation of the solubility product.

Table I. Solubility of Lithium Fluoride in Water

°C	Wt. %	°C	Wt. %
23.7	0.132	51.2	0.141
25.4	0.133	60.2	0.145
30.8	0.137	71.4	0.148
40.5	0.137	81.8	0.150
50.1	0.142		

EXPERIMENTAL

Approximately 12 grams of lithium fluoride (Lithium Corp. of America Lot 416-479, 7/7/71) were added to 1500 ml of distilled water (previously purged 1 hr with N_2) in a polyethylene bottle. The bottle was placed in a constant temperature bath capable of holding a selected temperature to 0.2°C. The solution was slowly mixed with a motor-driven, Teflon-coated stirrer. The bottle was capped with a plastic lid drilled to accept the stirrer shaft, a plastic thermometer well, and a rubber-stoppered opening for sample removal.

The bath temperature was first adjusted to a temperature several degrees above the desired temperature. The thermostat was then reset so that the temperature was slowly approached from the high side. The solution was then equilibrated for at least 24 hr at the selected temperature before withdrawing a sample for analysis. Solution temperature was read from a thermometer graduated to 0.2°C and inserted in the oil-filled thermometer well.

Filtered samples were obtained by drawing the solution into a 10-ml glass tube sealed to a glass frit of medium porosity. The sampler was warmed to approximately the solution temperature before sampling and after filling, and its contents were quickly poured into a tared plastic weighing bottle. After it was cooled and reweighed, the sample was diluted to 200 ml in a plastic volumetric flask, and the diluted solution was analyzed for lithium by flame photometry.

A Unicam Model SP-90 flame photometer operated in the emission mode with a Westronics Model YLS11B recorder was used for lithium determinations. An approximately 700-ppm lithium standard was prepared by dissolving 8.5 grams of lithium hydroxide monohydrate, neutralizing with dilute sulfuric acid, and diluting to 2 liters. The lithium content of this stock solution was accurately established by evaporating a 25-ml aliquot in a tared 50-ml platinum dish and weighing the ignited residue as lithium sulfate. Calibration was done each time samples were analyzed by measuring percent transmittances on 0–50-ppm lithium standards made by diluting appropriate amounts of the 700-ppm stock solution. Lithium results for samples were read directly from the flame photometer calibration curve. The average standard deviation (95% confidence limit) of results was 0.4%, relative, for four determinations made in duplicate.

Approaching the equilibration temperature from the low side was deemed unsatisfactory because in initial experiments lithium fluoride solubility results were found as much as 0.01% lower than results obtained when the temperature was approached from the high side.

Potentiometric fluoride determinations were made on several samples using the Orion fluoride electrode. Although these measurements gave calculated lithium fluoride solubility values about 0.005% lower than those calculated from flame photometric lithium determinations, unpublished work at our laboratories (*1*) has shown that lithium slightly interferes with the electrode measurements and could account for this small difference. The results of the fluoride measurements, however, were useful in showing that lithium fluoride apparently does not form an insoluble hydrolysis product that would give rise to a lithium:fluoride molar ratio in solution different from unity. Previous work in our laboratories (*3*) has shown that the amount of fluoride present would have a negligible influence on the flame photometric lithium results.

The solubility results reported in Table I appear to agree quite well with those reported by Payne in 1937 (*4*). He obtained lithium fluoride solubility values of 0.120, 0.133, and 0.135% for 0, 25, and 35°C, respectively. His measurements were made by weighing the residue of an evaporated sample.

For determinations in the presence of excess fluoride, 10.0 grams of LiF and 8.8 grams of $KF.2H_2O$ were added to about 1500 ml of nitrogen-purged distilled water. The solution was equilibrated at least 24 hr at 30.4°C after approaching the temperature from the high side. Samples were withdrawn in duplicate as previously described and analyzed for lithium and potassium by flame photometry. Fluoride determinations were made on these samples by the SPADNS [4,5-dihydroxy-3-(*p*-sulfophenylazo)-2,7-naphthalene-disulfonic acid, trisodium salt] colorimetric method (*2*). Calibration was accomplished over the range of 0–75 μg fluoride using appropriate aliquots of 5-ppm sodium fluoride standard. Measurements were made using a Bausch and Lomb Spectronic 20 spectrophotometer with fluoride results for samples read directly from a calibration curve. The average standard deviation of fluoride results was 0.4%, relative, for two determinations made in duplicate.

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Table II. Common Ion Effect on Lithium Fluoride Solubility

Description	Molarity Li^+	F^-	K^+
From Table I 30.8°C	0.0528	0.0528	...
Satd LiF + KF 30.4°C	0.028	0.0925	0.066
Satd LiF + LiCl 30.5°C	0.113	0.025	...

For determinations in the presence of excess lithium, 10.0 grams of LiF and 6.4 grams of LiCl were added to about 1500 ml of nitrogen-purged distilled water. The solution was equilibrated at 30.5°C for 96 hr after approaching the temperature from the high side. Samples were withdrawn in duplicate and analyzed for lithium and fluoride as before. The results are presented in Table II.

DISCUSSION

The solubility values of Payne are essentially verified by our measurements. The values up to 81.8°C show a slight increase in solubility.

An estimate of the heat of solution from the values at 23.7° and 81.8°C yields a value of 920 cal/mol ± 100 cal/mol.

The solubility products based on measurements from Table I are:

at 25°C	2.6×10^{-3}
at 80°C	3.3×10^{-3}

The data from Table II yields the following solubility products at temperatures between 30.4 and 30.8°C:

$$2.8 \times 10^{-3},\ 2.6 \times 10^{-3},\ \text{and}\ 2.8 \times 10^{-3}$$

These results show that within the range explored (doubling the cation or anion concentration), the counterion concentration can be calculated with reasonable accuracy and that knowledge of activity coefficients is not required.

LITERATURE CITED

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Vapor-Liquid Equilibria in Systems *n*-Hexane–Benzene and *n*-Pentane–Toluene

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Total vapor pressures of binary mixtures *n*-hexane–benzene and *n*-pentane–toluene were determined as functions of temperature and composition using a static method. The experimental results were correlated in terms of the Antoine equation. The interpolated isothermal P-x values were employed to compute equilibrium vapor compositions by means of an indirect method, in which the Redlich-Kister equation was used to represent the liquid activity coefficients. The P-x-y values thus obtained are presented for the *n*-hexane–benzene system at 30, 40, 50, and 60°C and for the *n*-pentane–toluene system at 20, 25, 30, 35, and 40°C.

Vapor-liquid equilibrium data for aromatic-saturated hydrocarbon mixtures are of interest to petroleum and petrochemical industries. These hydrocarbons are important constituents of the products from the catalytic reforming process. In this investigation, total vapor pressures for the binary systems *n*-hexane–benzene and *n*-pentane–toluene were experimentally determined by means of a static method. Vapor-liquid equilibrium data for the system *n*-hexane–benzene are available in the literature (*1*, *5*, *9*, *11*). However, isothermal data for the system were reported only at 25°C (*9*). The experimental results obtained were correlated by means of the Antoine equation from which isothermal *P*-*x* values were obtained. The equilibrium vapor compositions were then computed by an indirect method. The *P*-*x*-*y* values are presented at 30, 40, 50, and 60°C for the *n*-hexane–benzene system, and at 20, 25, 30, 35, and 40°C for the *n*-pentane–toluene system.

EXPERIMENTAL DETAILS

The arrangement of the apparatus is schematically shown in Figure 1. The main parts of the apparatus consist of an equilibrium cell and a solution reservoir. The equilibrium cell is made of a 100-ml flat-bottomed pyrex flask containing two small magnetic stirrers. The cell is connected to the manometer by a U-tube mercury seal-off valve (valve 1). This valve can be bypassed to the vacuum manifold or to the atmosphere by a three-way stopcock so that the mercury level in the U-tube can be manipulated. The solution reservoir is made of a 100-ml round-bottomed pyrex flask which can be isolated from the system by means of two U-tube mercury seal-off valves (valves 2 and 3). A capillary tube is connected to the upper

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