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CSSX

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**An Accelerated Rate Calorimetry Study of Caustic-Side Solvent Extraction Solvent
without Extractant**

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Summary

This study found that 4 - 48 part per thousand (ppth) of Caustic Side Solvent Extraction (CSSX) solvent without extractant in caustic salt solution at evaporator-relevant temperatures result in no process-significant energetic events. However, the data suggest a chemical reaction (possible decomposition) in the CSSX solvent near 140 °C. This concentration of entrained solvent is believed to markedly exceed the amount of solvent that will pass from the Modular Caustic Side Solvent Unit (MCU) through the downstream Defense Waste Processing Facility and enter the evaporator through routine tank farm operations. The rate of pressure rise at 140 °C differs appreciably – i.e., is reduced – for salt solution containing the organic from that of the same solution without solvent. This behavior is due to a reaction between the CSSX components and the salt solution simulant.

Introduction

The Modular Caustic Side Solvent Extraction Unit (MCU) will remove ¹³⁷Cs from Savannah River Site (SRS) caustic waste. The strip effluent stream from the MCU may entrain CSSX droplets on its way to the Defense Waste Processing Facility (DWPF). Operations within the DWPF can lead to transfer of the organic to the recycle stream that returns to the tank farms and eventually reaches the evaporators. Engineering personnel estimate that the evaporator temperature reaches a maximum of 160 °C near its steam coils (although in principle the temperature could approach the steam supply temperature of 190 °C). The combination of heat, caustic salt solution and organic might lead to undesirable conditions such as reaching the Lower Flammability Limit (LFL) of one of the CSSX components or generating gasses from a possible reaction between the CSSX components and the salt solution. A literature survey effort on the topic of heating organic containing caustic solutions can not rule out a possible reaction.¹ Therefore, SRNL personnel performed heating tests of caustic salt solutions containing expected levels of CSSX solvent.

Experimental Conditions

Personnel added 48 mg of CSSX solvent (without BobCalix)² to a 15 mL stainless steel vessel followed by 10 grams of 6 M Optima salt solution.³ (This amount exceeds the estimated concentration of organics expected in the 2H evaporator.) The vessel was attached to a pressure sensor (i.e., a sealed configuration with no chance for mass transfer with the outside) and inserted into an Accelerated Rate Calorimeter (ARC). The calorimeter was programmed to heat the sample from room temperature to 50 °C at a rate of 2 °C per minute under an air atmosphere. After reaching 50 °C, the sample temperature was increased in increments of 2 °C to the final program temperature of 170 °C (see Figure 1). Between each temperature increment, the instrument performed a heat and search mode. In the heat and search mode, the instrument monitors the self-heat rate

(dT/dt) of the sample determining if the sample self heats above a preset level (0.02 °C/min). The instrument maintains an adiabatic condition (with no sample heat loss to the environment) around the sample. The measured heat represents both the enthalpy associated with reactions or phase transitions as well as the heat capacity of the sample. The temporal variance of the heat can be used to determine the rate of the reaction and other thermal kinetic parameters (such as activation energy).

After the thermal test, personnel characterized the salt solution using FTIR analysis for organics and decomposition products. To sample the solution, personnel completely removed the solution from the ARC vessel and then removed small portions for analysis. Obtaining a representative sample proved difficult since the visual identification of the insoluble material (such as the CSSX solvent) in the salt solution was difficult.

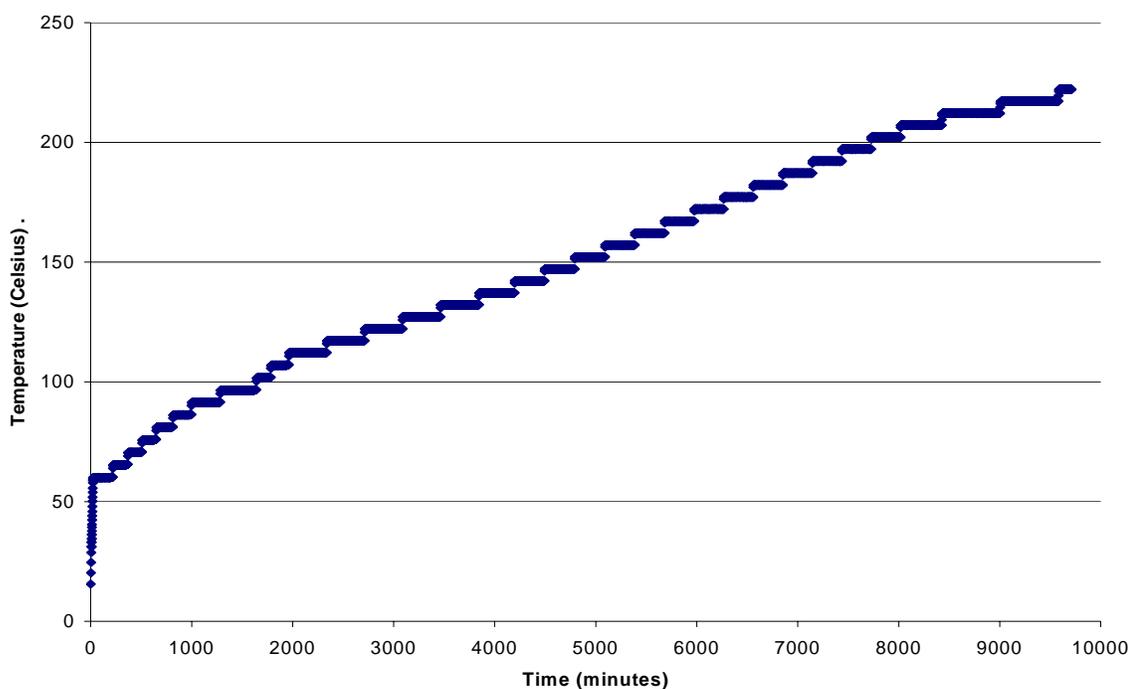


Figure 1. The temperature-time plot of the heating program employed to analyze the salt solution and the CSSX solvent.

Results and Discussion

Pressure-Temperature Behavior of Salt Solution at Constant Volume

Figure 2 shows the pressure versus temperature curve for salt solution with and without organics – i.e., Isopar[®] L, modifier (Cs-7SB), and trioctyl amine (CSSX without extractant). The shape of the curve for both the salt solution with and without CSSX organic shows a composite of two lines adjoining near 130 °C. However, the curve from the salt solution with 4 ppt CSSX organics shows a drastic break in the pressure data near 130 °C. This variation in pressure at 130 °C may be due to two possible mechanisms: 1) a kinetic effect (i.e., physical hindering of the salt solution boiling process) due to the presence of the organics on the surface of the salt solution, and 2) a chemical reaction between the organics and the salt solution. At 130 °C, the pressure rose instantaneously – some data is missing due to a difference between reaction and data collection speed – and is probably due to gas generation. We repeated the ARC experiment of the salt solution with CSSX organics but this time we increased the organic concentration to 48 ppt. Figure 3 shows the pressure-temperature relationship for this solution. As can be seen from Figure 3, we still see a break in the pressure data near 130 °C confirming the previous observation.

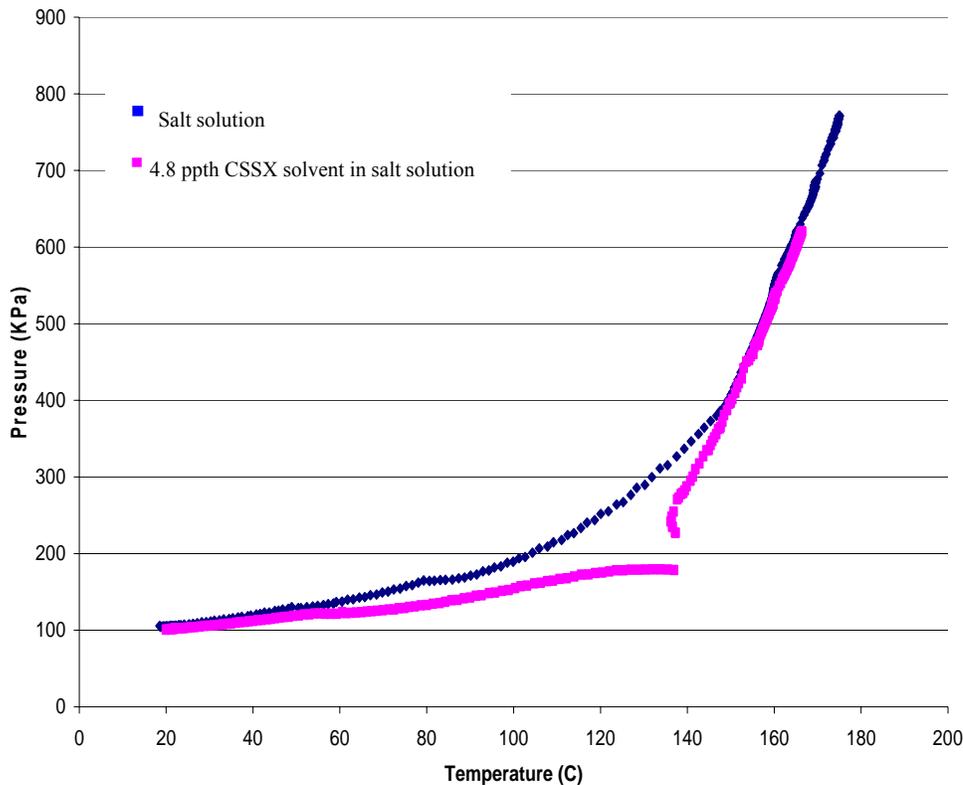


Figure 2. The pressure-temperature relationship for salt solution with and without CSSX organics.

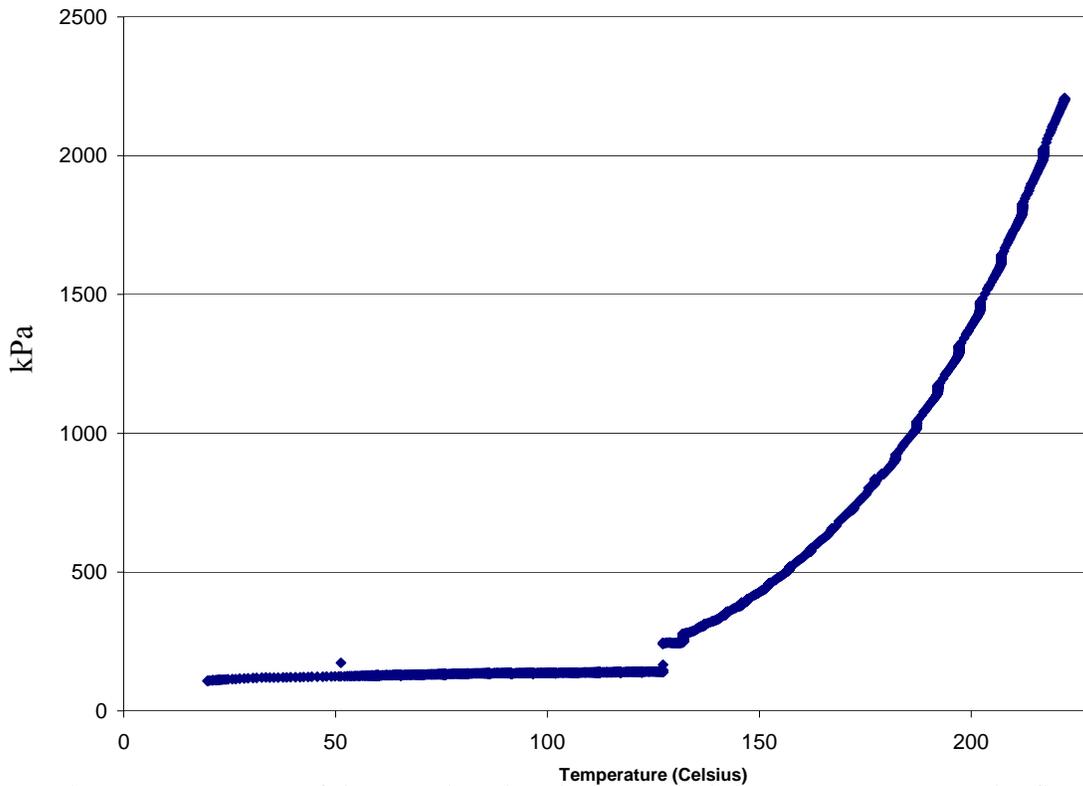


Figure 3. A repeat of the caustic salt solution containing 47 ppt CSSX. The figure shows a clear jump in the pressure data around 130 °C.

Both curves show negative curvatures with temperatures. The shape of both curves is distinct from the shape of the curve from the salt solution. The pressure curve from heating the salt solution should be given by the sum of the partial pressure of the salt solution vapor pressure and soluble gases in the solution.

$$P = \sum_{i=1}^n P_i$$

1

If we treat the salt solution vapor pressure to be similar to that of supersaturated water, we can estimate the vapor pressure and vapor mass above the salt solution with temperature. Table 1 list the calculated pressure, vapor volume, and mass from the steam tables for the test conducted in the ARC. Also shown in Table 1 is the pressure measured in the ARC with temperature for comparison. The calculated pressures are within 10% of

the measured pressures. This agreement is not surprising since salt solution vaporization is mainly water boiling.

Table 1. The predicted and measured pressures in the bomb containing salt solution as a function of temperature.

Temperature (°C)	Measured Pressure in the ARC (mPa)	Calculated Pressure* (mPa)	Vapor Volume* (mL)	Vapor Mass* (mg)
160	0.551	0.6178	4	13
175	0.779	0.771	3.82	17.45
190	1.104	1.254	3.6	23
220	2.136	2.207	3.14	36.4

*Calculated from the steam tables for a volume of 15 mL containing 10 grams of salt solution. C. A. Meyer, R. B. Mc Clintock, G. J. Silvestri and R. C. Spencer, "Steam Tables: Thermodynamic and Transport Properties of Steam," Sixth Edition, ASME 1997.

In the case of the salt solution containing CSSX organics the total pressure will also contain the vapor pressure from the CSSX components such as Isopar[®] L, tri-octylamine (TOA) and the modifier. Inspection of Figure 2 reveals the curve from the salt solution containing CSSX (at 4.8 ppth) overlaps the curve from the salt solution. Therefore, the pressure-temperature relationship for the salt solution is unaffected by the presence of trace levels of CSSX organics (except near 140 °C). The modifier and Isopar[®] L composition in CSSX is 29 and 69 wt % respectively. From the starting 48 mg of CSSX added to the bomb, we expect the bomb to contain 13.9 mg of Cs-7SB and 33.12 mg of Isopar[®] L. We also expect none (or negligible amount) of the CSSX components to be soluble in the salt solution. The solubility of the modifier (< 5 ppm), TOA (<0.04 ppm) and Isopar[®] L is negligible at room temperature.⁴ The vapor pressure of the Isopar[®] L, modifier and TOA is given in equations (Clayperon Equation) 2, 3,⁵ and 4.⁶

Isopar – L

$$P(Pa) = \exp\left(23.755 - \frac{5623}{T(K)}\right) \quad 2$$

Modifier

$$P(Pa) = \exp\left(32.202 - \frac{12154}{T(K)}\right) \quad 3$$

TOA

$$P(Pa) = \exp\left(26.817 - \frac{9781}{T(K)}\right) \quad 4$$

Figure 4 shows the pressure-temperature relationship for Isopar[®] L, modifier and TOA. Note the abscissa in Figure 4 is in the logarithm form.

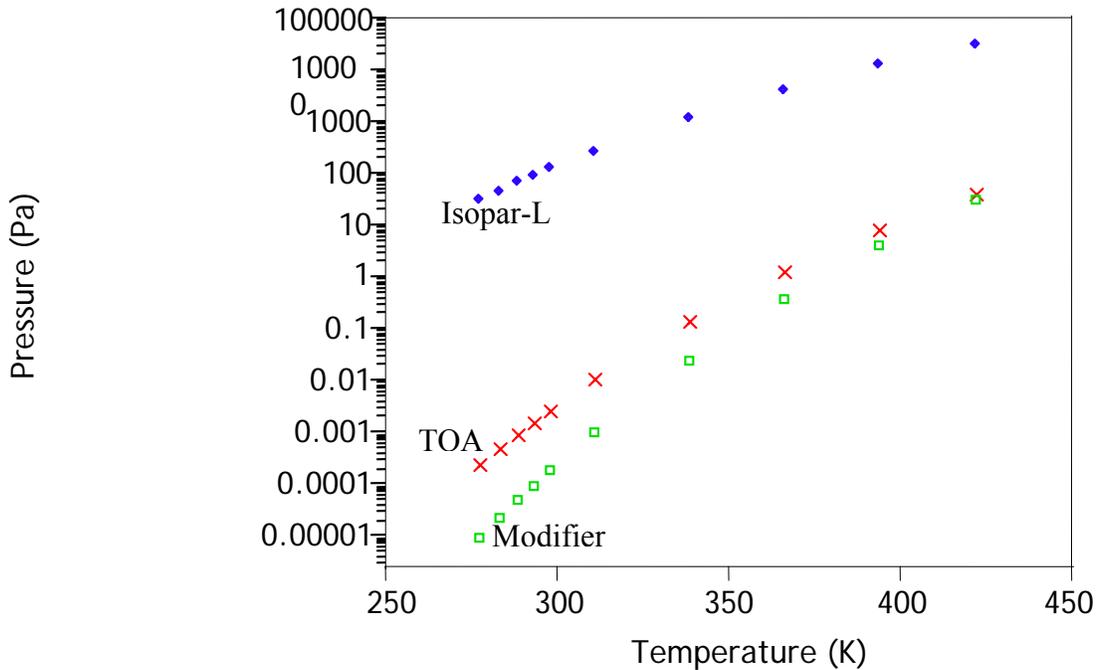


Figure 4. The pressure-temperature relationship for Isopar[®] L, modifier and TOA.

Another source of gases in the salt solution is the amount of soluble air in the 10 grams of salt solution. The gas amounts are negligible (8.1 μg of O₂ and 13.7 μg of N₂)⁷ and should play no role in the pressure of the system. We also expect all of the CO₂ absorbed in the salt solution to have reacted and become CO₃²⁻. We also assume very little N₂O or NO_x gas content in the salt solution.

Since Isopar[®] L, TOA and the modifier are under the vapor pressure of the salt solution in the bomb, we need to modify the vapor pressure of each component for the salt solution vapor pressure. The modification results in an enhancement of the vapor pressure of each according to equation 5.⁸ In this equation, $P_{component}$ is the pressure of the component under investigation. The term “ $P^{initial}$ ” is the initial pressure of the component. The final term v^{molar} is the molar volume of the component. The term Ln stands for the natural logarithm. The term “ RT ” is the multiplication of the gas constant R and the system temperature.

$$RT \ln \left(\frac{P_{component}}{P_{component}^{initial}} \right) = v_{component}^{molar} \times (P_{salt\ solution} - P_{component}) \quad 5$$

Assuming the vapor pressure of the modifier is negligible and the starting amount of TOA in CSSX is also negligible, the only component with appreciable gas pressure is the Isopar[®] L. Using a molar volume of 227 cm³/mol,⁹ we accounted for the effect of the salt solution vapor pressure on the gas pressure of Isopar[®] L.

Table 2. The enhancement effect on Isopar[®] L vapor pressure resulting from vaporization of salt solution.

Temperature (K)	Pressure (Pa) before Salt Solution Vapor Correction	Pressure (Pa) after Salt Solution Vapor Correction
433	4.75 E4	4.92 E4
448	7.34 E4	7.66 E4
463	11.0 E4	11.8 E4
493	23.1 E4	25.7 E4

Inspection of Table 2 reveals that the correction to the Isopar[®] L vapor pressure, due to the salt solution vapor, ranges from 5 to 11% and this factor increases further with temperature.

Another source of pressure rise in this test is due to the thermal expansion of the salt solution before boiling. The thermal expansion of water at 25 °C is 0.302 E-3 per 1 C. The solution expansion or gas volume compression is about 4% (from 25 °C to 140 °C). The calculated pressure rise resulting from the liquid thermal expansion is negligible compare to the pressure rise resulting from heating the vapor phase. Assuming no boiling or mass transfer between liquid and vapor phase, the compression of the gas from the expanding liquid only accounts for 0.1% of the pressure rise (see equation 6).

$$\left(\frac{\Delta P}{P}\right)^2 = \left(\frac{\Delta V}{V}\right)^2 + \left(\frac{\Delta T}{T}\right)^2; \left(\frac{\Delta P}{P}\right)^2 = (0.04)^2 + (0.4)^2 \tag{6}$$

Equation 6 is derived from taking the first derivative of the ideal gas law. Then taking the sum of squares (Pythagorean theory) to determine the change in pressure with changes in volume and changes in temperature.

$$vdp + pdV = nRdT \quad : \text{divide by } nRT$$

$$\frac{vdp}{nRT} + \frac{pdV}{nRT} = \frac{dT}{T}; \frac{dp}{p} + \frac{dV}{V} = \frac{dT}{T}$$

If all of the 33.12 mg of Isopar[®] L in our sample were to become gas in the 4 mL of empty space available (calculated in Table 1), the expected overall pressure (salt solution plus Isopar[®] L) is shown Table 3. Table 3 shows that the total pressure should be 40 to 20% greater, depending on temperature, than that measured by the ARC. This calculation indicates that some of the Isopar[®] L or the modifier is either reacting or becoming non-volatile (such as by solid formation) or it has become more soluble in salt solution at higher pressure and temperatures (than expected). If all the Isopar[®] L became soluble in salt solution at higher temperatures and pressures, then the calculated solubility is 0.4 wt %. The known solubility of Isopar[®] L in water is <0.01 % at 25 °C. It is conceivable that at 2.1 MPa most of the Isopar[®] L is in the salt solution. Another possibility is that the Isopar[®] L vapor molecules are adsorbed by a small film of silicon oil fluid (~ 2 mg) that covers and protect the pressure sensor. The pressure sensor monitors the bending of a thin metallic sheet. We apply a thin film of silicone oil to prevent corrosion of this metallic sheet. It is possible some of the Isopar[®] L vapor molecules were absorbed by this thin film. However, we do not foresee this mechanism as responsible for removing 33 mg of Isopar[®] L used in this experiment.

Table 3. Pressure calculations based on complete vaporization of Isopar[®] L in the bomb tested in this study. Measured pressure is shown for comparison.

Temperature (K)	Calculated Isopar [®] L Pressure if all Isopar [®] L volatizes(Pa)	Calculated Salt Solution Pressure (Pa)	Total Calculated Pressure (Pa)	Measured Pressure (Pa)	% Difference Between Calculated and Measured
433	1.76 E5	6.18 E5	7.93 E5	5.51 E5	44
448	1.9 E5	7.71 E5	9.61 E5	7.8 E5	23.4
463	2.1 E5	12.54 E5	14.6 E5	11.04 E5	32.5
493	2.55 E5	22.07 E5	24.6 E5	21.36 E5	15.2

We also measured the pressure-temperature relationship of the pure CSSX solvent. Figure 5 shows the pressure-temperature behavior (equilibrium) of CSSX solvent from room temperature to 250 °C. For this measurement, we placed 3 grams of CSSX solvent in a 10 mL stainless steel vessel. An inspection of Figure 5 shows that the system reached pressures greater than 400,000 Pascals. The figure also shows the pressure reached a near horizontal plateau or constant value from 150 °C to 200 °C. After 200 °C, the system pressure continued to rise. The slope of the P-T curve is proportional to the change in entropy (for example from liquid to gas) and inversely proportional to the molar volume change of the system. The zero-slope portion of the curve may be due to solid or a new liquid formation. If it is due to decomposition, then one of the Isopar[®] L or modifier components must have reacted to maintain constant pressure in the sample. An inspection of the temperature versus experiment time showed no exothermic or endothermic heat. It is worth noting that the flat slope in Figure 5 (which may suggest a chemical reaction in the pure CSSX solvent) occurs around the same temperature range

where the salt solution with CSSX solvent displayed a near zero slope line. Further work is needed in this area to understand the behavior observed.

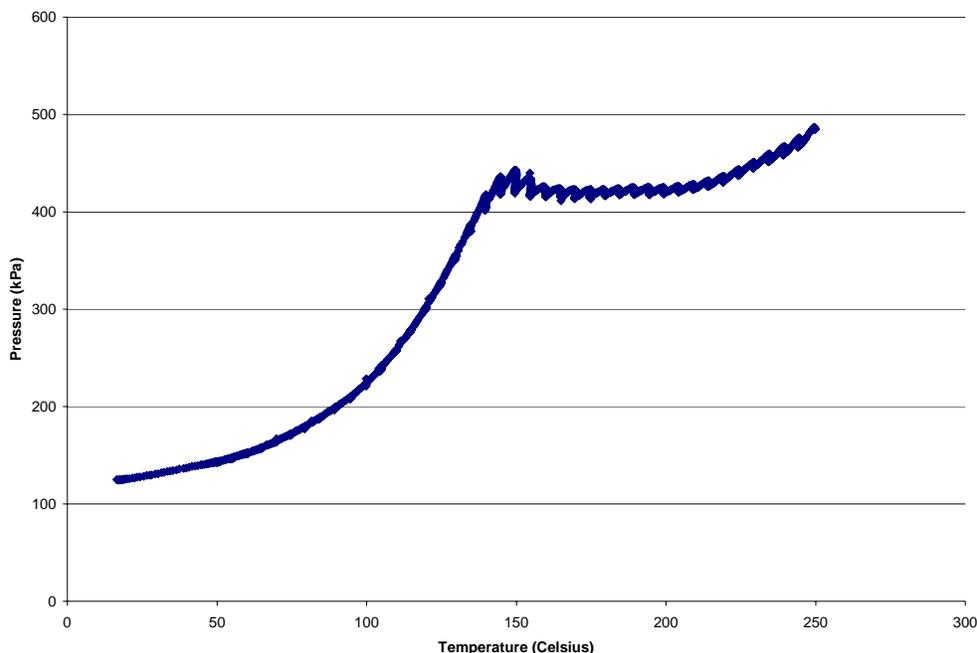


Figure 5. The pressure-temperature relationship for CSSX solvent.

Heat and Mechanical Energy Releases

For energetic reaction screening, we look for the magnitude of three variables: 1) dT/dt (the heat generation rate as deduced from the heat transfer rate), 2) dP/dt (the gas generation rate as this does work against the environment), and 3) the onset temperature.

Figure 6 shows the pressure rate as a function of temperature for salts solution with and without added organic. Inspection of Figure 6 shows that both salt solutions (with or without 4.8 ppt of CSSX) exhibit similar magnitude in pressure rise and their curves have similar shapes except near 140 °C. Therefore, there is not any energetic decomposition of substance – i.e., no substantial pressure surges – in the salt solution with CSSX organics. The step rise in the pressure rate data at 140 C from the salt solution with CSSX solvent corresponds to the pressure jump seen in Figure 2 but the magnitude of the gas expansion is bounded by the data for the salt solution without organics. The pressure rate break may be an indication of a possible reaction or solid formation.

Figure 7 shows the self-heat rate of the salt solutions with and without organics. The general increase from 50 to 130 °C in the self-heat rate is due to heat adsorption (i.e., heat capacity) and the sudden drop around 140 °C is due to a possible chemical reaction. Inspection of Figure 7 reveals no exothermic heat generation observed in this test for both solutions. Both curves extensively overlap over the temperature range. However, near 140 °C, the curve from the salt solution containing organics cooled a bit faster than the salt solution without organics as indicated by the sudden drop in self-heat. Again, this is consistent with the pressure data break in Figure 2.

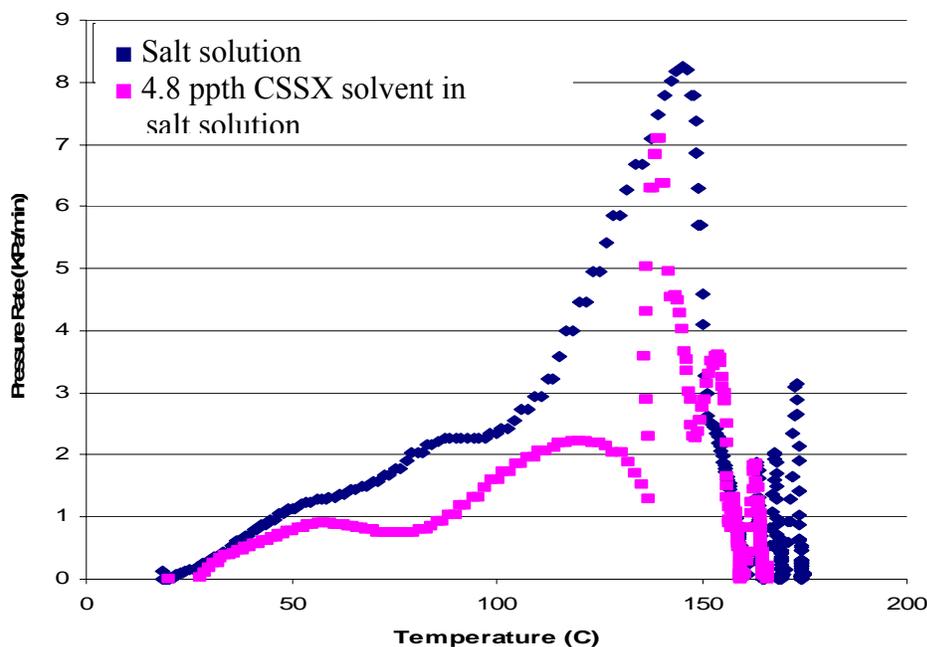


Figure 6. The pressure rate data as a function of temperature for salt solution with and without organics. Peak in the figures are an indication of reactions or decomposition.

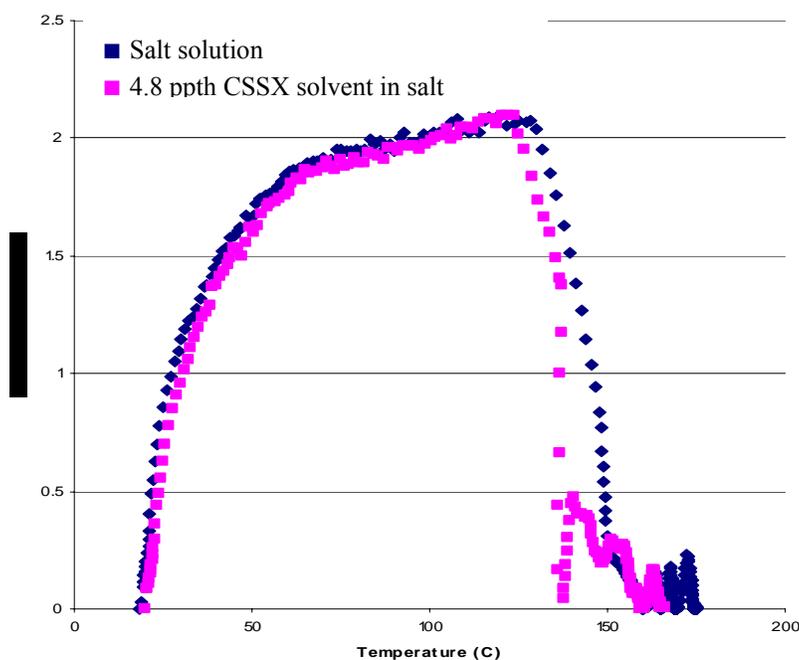


Figure 7. The self-heat rate of a caustic salt solution containing 4.8 ppt CSSX solvent. The figure also shows the self-heat rate of the caustic salt solution (Optima).

We attempted to measure the soluble organic composition remaining in the salt solutions after the heating test. We employed FTIR analysis to detect organics in the aqueous phase. However, due to low starting organic inventory, it was not possible to detect any organics by FTIR.

Conclusion

This study found that 4 - 48 part per thousand (ppth) of Caustic Side Solvent Extraction (CSSX) solvent without extractant in caustic salt solution at evaporator-relevant temperatures result in no process-significant energetic events. However, the data suggest a chemical reaction (possible decomposition) in the CSSX solvent near 140 °C. This concentration of entrained solvent is believed to markedly exceed the amount of solvent that will pass from the Modular Caustic Side Solvent Unit through the downstream Defense Waste Processing Facility and enter the evaporator through routine tank farm operations. The rate of pressure rise at 140 °C differs appreciably – i.e., is less than – for salt solution containing the organic from that of the same solution without solvent. This behavior is due to a reaction between the CSSX components and the salt solution simulant.

References

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- ¹ T. E. Britt, "Impact of CSSX Solvents and KTPB on Tank 50H Operation," Calculation Number X-CLC-H-00581, Rev. A, January 2006.
 - ² K. Adu-Wusu, D. D. Walker, T. L. White and S. L. Crump, "Preparation of Caustic-Side Solvent Extraction (CSSX) Solvent with BOBCalix6 for Wright Industries-Component Amounts, Analytical and Quality Assurance Results," SRNL-WPT-2005-00134, December 2005.
 - ³ D. D. Walker, "Composition of Simulant for Modular Caustic-Side Solvent Extraction Unit (MCU) Contactor Testing," SRNL-WPT-2005-0063, May 2005.
 - ⁴ B. A. Moyer, S. D. Alexandratos, P. V. Bonnesen, G. M. Brown, J. E. Caton, Jr., L. H. Delmau, C. R. Duchemin, T. J. Haverlock, T. G. Levitskaia, M. P. Maskarinec, F. V. Sloop, Jr., and C. L. Stine, "Caustic-Side Solvent Extraction Chemical and Physical Properties Progress in FY 2000 and FY 2001," ORNL/TM-2001/285, February 2002.
 - ⁵ W. V. Steele, "Vapor Pressure of 1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol," ORNL/TM-2001/287, January 2002
 - ⁶ W. V. Steele, R. D. Chirico, S. E. Knipmeyer, A. Nguyen, N. K. Smith, and I. R. Tasker, "Thermodynamic Properties and ideal-Gas Enthalpies of Formation of Cyclohexene, Phthalan dihydrobenzoFuran, Isoxazole, Octylamine, Dioctylamine, Trioctylamine, Phenyl Isocyanate, and Tetrahydropyrimidine," J. Chem. Eng. Data 1996, 41 (6), pp 1269-1284.
 - ⁷ T. Hang and D. D. Walker, "Gas Generation and Bubble Formation Model for Crystalline SilicoTitanate Ion Exchange Ion Exchange Columns," WSRC-TR-2000-00177, June 2000.
 - ⁸ W. T. Moore, "Physical Chemistry," 3rd edition, Prentice Hall, 1962.
 - ⁹ L. H. Delmau, T. J. Haverlock, T. G. Levitskaia, F. V. Sloop, Jr., and B. A. Moyer, "CSSX Chemical and Physical Properties: Equilibrium Modeling of Distribution Behavior," ONRL/TM-2001/267, December 2001.