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Media or Heat Exchanger Fluids

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FROM: C. H. Seow

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594 001

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1

CONCENTRATED SALT SOLUTIONS FOR
REACTOR FUEL MEDIA OR HEAT EXCHANGER FLUIDS

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Summary

The vapor pressures of several concentrated salt solutions have been measured over the temperature range from 200 to 400°. Solutions of either LiNO_3 or $\text{Ca}(\text{NO}_3)_2$ show some promise for application as primary heat transfer media for solid fuel element reactors as well as for a fuel bearing material for homogeneous reactors.

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It has been suggested that aqueous salt solution might be of interest as heat transfer agents for use in atomic power reactors. Presumably, by dissolving a salt in water, the vapor pressure of water could be lowered sufficiently such that power removal operations could be carried out at higher temperatures and still not exceed a particular maximum pressure limitation. The higher operating temperature would result in greater thermodynamic efficiency, provided other properties of the water-salt system were favorable or, if unfavorable, were offset by the higher available temperature.

It is perhaps possible that concentrated aqueous salt solutions could be adapted for use in homogeneous reactors utilizing either solutions or slurries. For example, soluble uranium salts could be dissolved in a high concentration aqueous salt solution to produce a final solution of low

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594 002

vapor pressure. Such a system might also alleviate the problem of hydrolytic precipitation characteristic of very dilute uranyl salt solutions. As another alternative, concentrated aqueous salt solutions could well provide stable media for the suspension of insoluble UO_3 or ThO_2 to form slurries capable of fueling a reactor. These slurries would possess considerably lowered vapor pressures compared to pure water-solid slurries. In addition, the higher viscosities and the electrolytic character of the aqueous salt solution-solid suspension might possibly tend to stabilize the suspension, thereby reducing overall settling rates. Also, the higher viscosity of the mixture compared to water might tend to reduce erosion effects caused by the suspended solid particles. In other words, the solid particles might be "cushioned."

There is a good possibility that aqueous salt heat transfer systems will be radiation and thermally stable as contrasted to the radiation and thermal decomposition of organic liquids, i.e., diphenyl and others, at high temperature. In comparison to fused salt systems, which are solids at room temperature, aqueous salt solutions can be selected which are liquid from 25° to temperatures above 400°C . In addition, an appreciable concentration of moderator is present as hydrogen or deuterium constituents of water thus providing suitable conditions for thermal reactors.

The purpose of this investigation was to select and explore several aqueous salt systems with respect to vapor pressure lowering. Several factors were considered in their selection as follows: The salt selected must show sufficiently high solubility in water throughout the high temperature range. A high solubility is necessary to obtain a sufficient

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594 003

vapor pressure lowering. Several salts, which otherwise appear attractive, have not been studied because they almost certainly undergo sufficient hydrolysis to yield precipitates at elevated temperatures. Among these are zirconium and beryllium compounds. It is desirable, but not necessary, that the water-salt system be liquid at room temperature. The salt must have sufficient thermal and radiation stability in water and the nuclide components of the salt must have low neutron absorption cross sections and must not produce highly radioactive daughter nuclides. In addition, the usual properties of heat exchanger fluids such as viscosity, heat capacity, thermal conductivity, and density, must be considered.

With these factors in mind, several aqueous salt systems were selected for vapor pressure measurements. These systems were (1) 3.8 molal Li_2SO_4 plus 3.8 molal UO_2SO_4 (combined solution), (2) Li_2SO_4 (sat'd), (3) MgSO_4 (sat'd), (4) 50.0 wt. % LiNO_3 and (5) several $\text{Ca}(\text{NO}_3)_2$ solutions.

The experimental data were obtained by direct measurement of vapor pressure using, in most of the runs, a precision Heise pressure gauge. Data for all systems studied are comparatively shown in Tables 1 and 2 and in Figure 1. Experimental data were obtained at every 2 to 5 degree interval; however, in Figure 1 and in the tables, only the data at approximately 10 degree intervals are given. The actual vapor pressure can be obtained by multiplying the ratio, p/p_0 , where p = expl. pressure and p_0 = sat'd. steam pressure, by the vapor pressure of saturated steam at the particular temperature.

The data indicate no large changes of p/p_0 as a function of temperature at least up to 400°C . It is not certain at this time whether the small

TABLE 1

Vapor Pressure Data of Several Salt-Water Systems

LiNO ₃ 50.0 Wt. % (14.5 molal or 0.207 Mole Fraction)		3.8 Molal Li ₂ SO ₄ 3.8 Molal UO ₂ SO ₄		LiSO ₄ (sat'd)		MgSO ₄ (sat'd)	
t°C	p/p _o *	t°C	p/p _o	t°C	p/p _o	t°C	p/p _o
214	0.407	220	0.71	240	.97	225	.92
220	.407	225	.70	245	.90	235	.92
225	.405	230	.73	248	.88	245	.91
230	.402	240	.72	250	.91	256	.98
234	.401	245	.73	252	.94	260	.96
238	.399	250	.74	260	.95	262	.97
243	.399	255	.75	265	.96	267	.95
250	.399	260	.75	270	.97	275	.94
254	.405	270	.78	275	.98	281	.96
259	.403	275	.79				
270	.407	280	.81				
275	.406	285	.81				
280	.408						

*p_o = pressure of saturated steam. (Osborne and Myers, U. S. Bureau of Standards).

p = experimental pressure of the solution.

5

TABLE 2

Vapor Pressures of $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ Solutions

69.5 wt. % (13.8 molal or 0.20 mole fraction)		61.6 wt. % (9.80 molal or 0.15 mole fraction)		50.3 wt. % (6.17 molal or 0.10 mole fraction)		37.7 wt. % (4.50 molal or 0.075 mole fraction)		32.4 wt. % (2.92 molal or 0.05 mole fraction)		0 wt. % (pure water)	
t°C	p/p ₀	t°C	p/p ₀	t°C	p/p ₀	t°C	p/p ₀	t°C	p/p ₀	t°C	p/p ₀
200	.413	200	0.622	201	0.622	204	.898	200	0.942	200	1.000
212	.417	211	.603			217	.888	212	.930	210	1.014
222	.432	222	.571	212	.656	228	.869	222	.943	225	1.000
234	.411	234	.569			239	.832	230	.953	235	1.004
250	.407	246	.575	222	.657	247	.848	238	.959	245	1.007
264	.420	250	.575	228	.665	257	.838	246	.968	250	1.009
278	.421	258	.589	238	.672	271	.838	250	.967	260	1.013
297	.435	266	.593	245	.679	283	.819	258	.974	270	1.006
313	.436	274	.600	250	.679	292	.810	266	.973	280	1.010
322	.437	282	.604	260	.687	313	.810	278	.972	290	1.002
330	.434	290	.608	273	.695	319	.804	286	.963	300	1.005
336	.434	298	.609	280	.706	334	.802	294	.961	310	1.008
340	.434	306	.607	290	.701	340	.806	300	.951	320	1.002
347	.433	314	.606	300	.699	354	.790	308	.948	330	1.007
350	.434	322	.602	310	.699	360	.783	318	.935	345	.999
355	.428	330	.600	321	.696	370	.783	324	.927	350	1.002
360	.425	338	.577	330	.691			332	.922	360	1.006
365	.428	348	.573	340	.692			340	.911	370	1.012
370	.426	358	.542	350	.686			348	.901	374	1.018
		368	.545	360	.683			356	.891		
		370	.544	370	.678			365	.883		
		380	.54*	380	.67*			372	.879		
		388	.54*	390	.68*			380	.88*		
				400	.67*			390	.88*		
								400	.88*		

* Using extrapolated values for p₀.

594 006

changes of p/p_0 with temperature for each particular curve are significant or whether they are due to inaccuracies arising from experimental techniques. The solution concentrations are those at room temperature and do not represent the true concentration at the high temperature. The high temperature concentrations, however, should not differ from the room temperature value by more than several percent at the highest temperature.

In Figure 2, p/p_0 measured at 350° is plotted as a function of the mole fraction of $\text{Ca}(\text{NO}_3)_2$. A mole fraction of 0.2 corresponds to the stable solid hydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, at room temperature. This solid melts at 42.7°C . to form a liquid which is apparently stable to above 400°C . A slight orange-red vapor phase coloration is observable in sealed silica tubes in the temperature range 450 - 500°C . thus indicating some decomposition of the nitrate to nitrogen oxides. Lithium nitrate-water solutions apparently are as stable as $\text{Ca}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. A 50.0 wt. % LiNO_3 solution is liquid from room temperature to above 400°C .

Figure 3 indicates the possible increase in operating temperature for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ liquid over that of pure water at a particular temperature and pressure. For example, at 350°C . at a saturated steam pressure of 2398 p.s.i., $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ liquid could be used at 412°C . (i.e., $350^\circ + 72^\circ$) at the same vapor pressure. Since the line in Figure 3 is essentially straight it can be represented by the equation, $\Delta t = 0.1875t + 7.00$.

In conclusion, favorable vapor pressure lowering could be achieved using concentrated aqueous salt solutions which might indicate possible advantages to be attained over pure water, organic, and fused salt heat transfer agents. It would remain to be seen how the other heat transfer factors and the radiation stability would compare to these other liquid media after considering the differences in allowable operating temperatures and in the other factors.

FIGURE 1

VAPOR PRESSURE RELATIONSHIPS OF SEVERAL AQUEOUS SALT SOLNS

p = pressure of the solution

p_0 = saturated steam pressure

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FIGURE 2
VAPOR PRESSURE RELATIONSHIPS OF $\text{Ca}(\text{NO}_3)_2$ - H_2O SOLNS AT 350°C
 p = p.s.i. of salt soln
 p_0 = p.s.i. of satd steam
 (2398 p.s.i. at 350°C)

8

10

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FIGURE 3

COMPARISON OF $(t_{\text{salt soln}} - t_{\text{H}_2\text{O}})$ AT CONSTANT PRESSURE FOR 69.5 wt % $\text{Ca}(\text{NO}_3)_2$

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