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Short communication

Testing of crystallization inhibitors in industrial LiBr solutions

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Abstract

Concentrated lithium bromide (LiBr) solutions are used in absorption heat pumps for heating and cooling buildings. To increase the Carnot efficiency of heat pumps, it is necessary to decrease the lowest temperature of the cycle while keeping the high concnentration LiBr solution from freezing. By adding the appropriate additive, the crystallization temperature can be decreased to allow the enlargement of the operating range. As an attempt to test the behavior of several organophosphorous additives within industrial LiBr solutions, the freezing points of unused and used industrials solutions in the presence of these additives have been measured. The temperature stability of the tested additives has also been determined. © 2001 Elsevier Science Ltd and IIR. All rights reserved.

Keywords: Absorption system; Liquid chiller; Water/lithium bromide; Solution; Crystallization-inhibition; Chemical product

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Inhibiteurs de cristallisation dans les solutions de LiBr : essais

Résumé

On emploie des solutions de bromure de lithium (LiBr) concentrées dans les pompes à chaleur à absorption utilisées pour chauffer et refroidir les immeubles. Afin d'augmenter l'efficacité du cycle Carnot des pompe à chaleur, il faut diminuer la température la plus basse du cycle tout en empêchant la congélation de la solution concentrée de LiBr. On peut diminuer la température de cristallisation à l'aide de l'ajout d'un additif approprié, permettant ainsi d'élargir la gamme de fonctionnement. Les auteurs ont mesuré les points de congélation des solutions de bromure de lithium industrielles déjà employées ou non, afin d'étudier leur comportement en présence de plusieurs additifs organophosphorés. On a également déterminé la stabilité, à la température utilisée, des additifs testés. © 2001 Elsevier Science Ltd and IIR. All rights reserved.

Mots clés : système à absorption ; refroidisseur de liquide ; eau/bromure de lithium ; solution ; cristallisation ; inhibition ; produit chimique

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Lithium bromide aqueous solution is an essential ingredient in the operation of absorption heat pumps that are used for heating and cooling whole buildings. Water is evaporated and condensed from LiBr solution which is the refrigerant analogous to freon in compressive heat pumps [1] while the LiBr solution acts as the compressor at different temperatures and concentrations. Like any heat engine cycle, the Carnot efficiency is given by difference in the high and low temperatures

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divided by the high temperature [2], $\eta = (T_H - T_L/T_H)$. The LiBr solution and its water vapor can reach temperatures as high as 98, 177 and 232°C depending on the machine type while the lower temperature the LiBr solution and its water vapor can reach are typically 4–7°C for cold air conditioning. At this coldest temperature, the LiBr solution is close to the crystallization point as the solubility of LiBr in solution decreases with decreasing temperature. The efficiency of the heat pump can be increased if the crystallization temperature can be decreased keeping the LiBr concentration the same. Most manufacturers operate with a margin of safety since there are massive difficulties to clear the piping system when the solution crystallizes.

By adding the appropriate additive to the LiBr solution, this crystallizing temperature can be decreased allowing the enlargement of the operating range. The freezing point of concentrated LiBr solutions depends upon their concentration since different solids (e.g. ice, tri-, di- and mono- hydrates of LiBr) are produced according to the concentration of the LiBr solution. When cooled, a concentrated LiBr solution, like all particulate free salt solutions, does not freeze at the equilibrium freezing point but at a temperature below the equilibrium freezing point, due to the need to supersaturate the solution before nucleation can take place [3]. This temperature difference is called the Ostwald–Meyers meta-stable zone. Each type of solution has a different width for its meta-stable zone. The effect of crystallization inhibitors at a concentration of 500 ppm on the LiBr crystallization temperature has been studied [4]. Some of these additives further decreased the crystallization temperature by up to 13 K below the experimental freezing point. Large decreases in the crystallization temperature could be correlated with large values of complexation constants of the additive for either the Li^+ or the Br^- ion in solution. Solution complexation, however, is not sufficient to explain the magnitude of the decrease in the crystallization temperature: this has been quantitatively justified by the additive adsorption at the crystal/solution interface, altering the surface energy. The Dequest® organophosphorous additives were among the most efficient additives. These additives have been extensively used as calcium sulfate or calcium carbonate scale inhibitors [5].

As an attempt to test the behavior of these additives within industrial LiBr solutions, the freezing point of unused and used industrial solutions in the presence of some additives that showed the most efficient with clean LiBr solution [4] has been measured. The temperature stability of the tested additives has also been determined since the LiBr solution is heated to 98, 177 and 232°C for single, double and proposed triple effect machines, respectively: the additives will need to remain stable at these temperatures.

Four liters of two LiBr solutions were kindly supplied by Trane Inc. One of them had been used in an absorption heat pump: the other was an unused solution. Both of these solutions contained corrosion inhibitors, i.e. ~300 mg/l molybdate and 0.08±0.02 alkalinity as LiOH. The used solution also contained insoluble black material which was attracted to a magnet — probably magnetite, Fe_3O_4 according to Trane Inc. Extra LiBr was added to these solutions in order to increase the concentration to 60 wt.% (first series) and to about 61 wt.% (additional experiments). Dosing the LiBr was difficult because of the presence of the LiOH. Our technique relied on matching the refractive index of these solution to the corresponding concentration of LiBr pure solution [6–7]. The freezing point of the new and the used industrial solutions were tested with several additives: pyrophosphoric acid (PPA, technical grade, Aldrich Chemical Co., Milwaukee, WI, USA), methylene diphosphoric acid (MDPA, 98%, Aldrich Chemical Co.), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP, Dequest® 2010, Monsanto Chemical Co., St Louis, MO, USA), aminotri(methylenephosphonic acid) (ATMP, Dequest® 2000, Monsanto Chemical Co.), diethylenetriaminepenta(methylene phosphonic acid) (DTPMP, Dequest® 2060, Monsanto Chemical Co.) and 5-amino-2,4,6-trioxo-1,3-perhydrodizine-*N,N*-diacetic acid (uramil-*N,N*-diacetic acid, >99.0%, PFaltz & Bauer Inc., Waterbury, CT, USA). The industrial solutions were also tested without additive as a reference measurement. The freezing temperature measurements were carried out according to a previously described methodology [4].

Table 1 shows a comparison of the freezing point temperature between the industrial solutions and the pure LiBr solutions previously tested [4]. The results with the new industrial solution were not significant with the HEDP additive but showed some crystallization inhibition with the MDPA additive at 500 ppm. Part of the problem with using this solution was the analytical methods used to assay the LiBr content of the solution provided. It is believed that this solution has a lower concentration than desired and these results are biased accordingly. The results of the used industrial solution appear to be more closely assayed to 60 wt.% LiBr pure solution. Both the HEDP and MDPA additives were effective as crystallization inhibitors with MDPA being the best. Using 500 ppm of MDPA, the insoluble black material dissolved forming a transparent ruby red colored solution. It is believed that some of the MDPA was used to complex the magnetite and as a result the remaining MDPA is not as effective in used industrial solution as it is in pure LiBr solution (see Table 1 for comparison). These results are encouraging for industrial tests of these crystallization inhibition additives.

Additional tests were performed with new and used industrial solutions doped with LiBr to reach 61.27 and

61.05 wt.% LiBr, respectively. In these tests, the additive concentrations were chosen at their maximum effectiveness when measured with clean solutions [4]. For the new industrial solution, 250 ppm of MDPA showed no effect on LiBr freezing temperature, 750 ppm of PPA and 1500 ppm of HEDP showed minor effects, 1500 ppm of ATMP and 1500 ppm of Uramil had more influence and 1500 ppm of DTPMP was the most efficient. With the used industrial solutions, 250 ppm of MDPA had the lowest effect, 750 ppm of PPA and 1500 ppm of ATMP had intermediate effect and 1500 ppm of Uramil, HEDP and DTPMP were the most efficient. These results are in contrast to the previous results with lower concentrations of MDPA and HEDP where MDPA was more effective than HEDP. Similar trends, however, were observed between the new industrial solutions and used industrial solutions.

It is clear that the results obtained with the new industrial solution are not as good as those of the used industrial solution for both HEDP and MDPA shown in Table 1 and all additives shown in Table 2. This is mainly due to the presence of about 300 ppm molybdate in the new industrial solution which is also complexed by the additives, removing them from solution and diminishing their activity. Concerning the used solution, most of the molybdate corrosion inhibitor is not present

Table 1
Freezing point of industrial solutions with and without crystallization inhibitor additives. Comparison with results obtained with stock solutions

Tableau 1
Points de congélation de plusieurs solutions industrielles avec et sans l'ajout d'additifs inhibiteurs de cristallisation. Comparaison avec les résultats obtenus avec les solutions commercialisées

Solution	Measured freezing point from industrial solutions (°C)	Freezing point from stock solutions [(°C)± S.D.][a]
New industrial solution — no additive	+0.8	+3.3±0.44
With 500 ppm HEDP	+0.7	−6.15±7.49
With 500 ppm MDPA	−2.0	−10.16±3.17
Used industrial solution — no additive	+3.8	+3.3±0.44
With 500 ppm HEDP	−3.0	−6.15±7.49
With 500 ppm MDPA[b]	−8.8	−10.16±3.17

[a] Measurements performed in (4), LiBr concentrations was 60.54 wt.%.

[b] Black material dissolved giving ruby colored solution.

Table 2
Freezing point of industrial solutions with and without crystallization inhibitor additives at the concentration corresponding to their maximum effectiveness (in pure LiBr solutions)

Tableau 2
Points de congélation de plusieurs solutions industrielles avec et sans l'ajout d'additifs inhibiteurs de cristallisation à la concentration à laquelle leur efficacité est maximale (pour des solutions de LiBr pures)

Solution	Freezing point [(°C)±S.D. (K)]
New industrial solution — no additive (61.27 wt.% LiBr)	+8.09±1.34
250 ppm MDPA	+7.43±1.56
1500 ppm HEDP	+5.72±2.56
750 ppm PPA	+5.31±0.86
1500 ppm ATMP	+2.95±1.37
1500 ppm Uramil-*N,N*-diacetic acid	+1.59±0.50
1500 ppm DTPMP	−5.18±5.21
Used industrial solution — no additive (61.05 wt.% LiBr)	+13.15±4.64
250 ppm MDPA	+6.87±0.63
1500 ppm ATMP	−1.28±4.63
750 ppm PPA	−3.67±4.15
1500 ppm Uramil-*N,N*-diacetic acid	−7.75±1.87
1500 ppm HEDP	−9.39±4.93
1500 ppm DTPMP	−10.07±5.07

Table 3
Thermal decomposition temperatures for crystallization inhibitors

Tableau 3
Températures de décomposition thermiques des inhibiteurs de cristallisation.

Additive	LiBr concentration (wt.%)	Decomposition temperature(s) (°C)
MDPA	60.54	200 230–400 (broad)
PPA	60.82	95
ATMP	60.82	150 200–400 (broad)
DTPMP	60.82	240 320 (broad)
HEDP	60.82	205 360 (broad)
Uramil-*N*,*N*-diacetic acid	60.54	210 240 (broad)

any more allowing the crystallization inhibitor to fully play its role. The use of crystallization inhibitors as a molybdate complexing agent could be used as a reservoir to release slowly both the molybdate when it is required for corrosion inhibition, and the crystallization inhibitor at the same time. This concept should be tested in an industrial absorption heat pump to be demonstrated.

Since the LiBr Solution can be heated up to 232°C depending on the absorption heat pump used, the additives will need to be stable to these temperatures in order to be efficient for the following cooling cycle. The additive PPA decomposes in hot (95°C) water to H_3PO_4. The other additives underwent thermal decomposition using a scanning thermogravimeter in an inert helium atmosphere with a temperature ramp rate of 20°C/min. The results presented in Table 3 indicate that they are thermally stable to temperatures above 200°C making them viable candidates for crystallization inhibitors in two cycles LiBr adsorption heat pumps.

In conclusion, it was shown that the strongest crystallization inhibition additives tested in industrial LiBr solutions have performed as expected. In addition, the thermal decomposition temperatures of these additives are above 200°C in most cases indicating that they will survive passage through the high temperature generator of the absorption heat pump cycle. The results are sufficiently encouraging to warrant industrial tests of these crystallization inhibitor additives.

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