XVIII[e]
CONGRÈS
INTERNATIONAL
DU FROID

18
IIF-IIR-MONTRÉAL-1991

XVIII[th]
INTERNATIONAL
CONGRESS OF
REFRIGERATION

Volume II

Les actes du XVIII[e] Congrès international du froid

10-17 août 1991, Montréal (Québec) Canada

Le froid sans frontières

Proceedings of the XVIII[th] International Congress of Refrigeration

August 10-17, 1991, Montréal, Quebec, Canada

New Challenges in Refrigeration

FLUIDS FOR ABSORPTION MACHINES : EXPERIMENTAL DATA AND WORKING PERFORMANCES.

Mauro FELLI, Franco COTANA, Cinzia BURATTI

Istituto di Energetica, Universita' di Perugia
Via Cairoli, 24 - 06100 Perugia - Italy

1. GENERAL FEATURES

Methanol-Salt solutions were proposed in the Literature as working fluids for absorption refrigerating machines since about 1940 [1]; they had no relevant development in commercial engines but, nevertheless, researches have continued until today [2] . That may be explained because these fluids look attractive for absorption refrigeration: if compared with Water-Lithium Bromide, they show about the same advantages: no rectification, very high solubility, high heat of vaporization, also if lower than that of Water. Moreover, they allow to reach evaporating temperatures below 0 °C (the triple point of Methanol is -97.7 °C), that is not possible with Water-Lithium Bromide.

In the present work the ternary mixture Methanol-Lithium Bromide-Zinc Bromide is considered. In the Literature it is possible to find data on the thermophysical properties of this mixture only for a fixed value of the molar ratio between the two salts (2:1, that means two moles of LiBr for one mole of $ZnBr_2$). We have extended the research to the molar ratios 3:1 and 1:2, in order to investigate how the values of the thermophysical properties vary and to individuate, if any, the most favourable mixture for use in absorption machines. Besides the ratio 2:1 is also considered and the results compared with the data from Literature.

The following properties have been determined: vapour pressures, specific heat, kinematic viscosity, density. The experimental values have been then introduced in a computer program, in order to evaluate the performances of each mixture with reference to a basic refrigerating cycle; a comparison has been also made with the performances of the mixture Water - Lithium Bromide.

2. SUBSTANCES AND MIXTURES

The used Methyl Alcohol is produced by Carlo Erba S.R.L., Milan, Italy; purity: >99.9%; principal impurity: Water (<0.08%). Lithium Bromide and Zinc Bromide are produced by Merck, Darmstadt, F.R.G.; purity: >99%; principal impurities : Chlorine (<0.1%), Iodine (<0.02%).The mixtures have been prepared according to a procedure described in a previous work [3]. The molar ratios 2:1, 3:1, 1:2 between LiBr and $ZnBr_2$ have been considered. For each molar ratio, samples were prepared for mass concentrations of Methanol of 40%, 50%, 70%, 90%. Each sample was prepared in a quantity large enough to complete all the experimental procedures (about 500 gr for each sample).

3. VAPOUR PRESSURES

The experimental apparatus and procedure were described in a previous work [4]. The P-T-X curves have been determined on samples of solution at fixed concentration; the temperature of the sample is varied and contemporary measures of pressure and temperature are operated. The apparatus [4] has been improved with the utilization of a data logger, so that the P-T-X curves are automatically sketched. On the average, six experimental points are determined for each sample at fixed concentration: the results are reported in table 1. The experimental data may be correlated by means of the Antoine equation:

$$\log P = A - B/T \qquad (1)$$

The constants A and B are determined as functions of the mass concentration X, for the mixtures having ratios 2:1, 3:1 and 1:2 between the moles of LiBr and $ZnBr_2$ within the solution; so the P-T-X diagrams of figg. 1, 2, 3 can be sketched. A general tendency

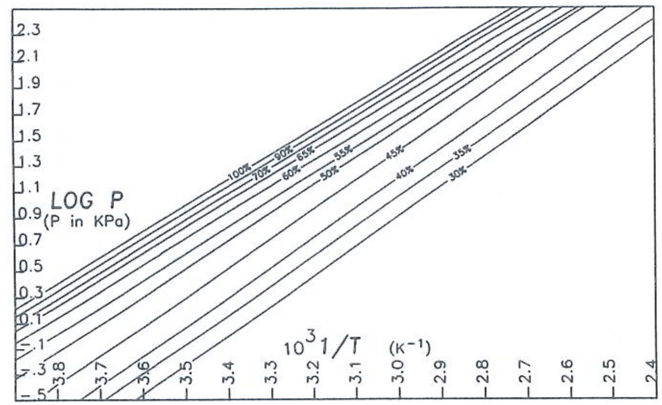

Fig.1 - P-T-X diagram of the mixture CH_3OH-LiBr-$ZnBr_2$ (2:1)

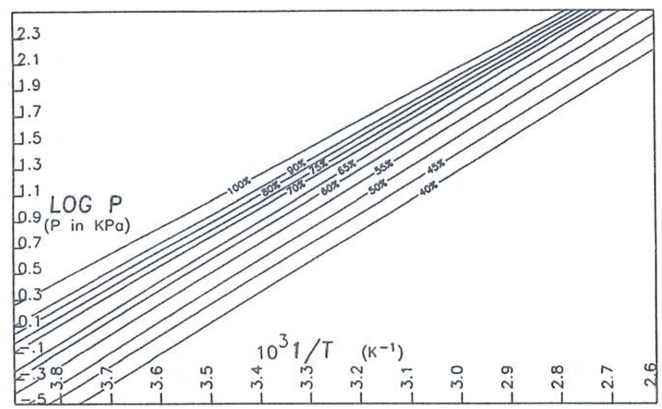

Fig.2 - P-T-X diagram of the mixture CH_3OH-LiBr-$ZnBr_2$ (3:1)

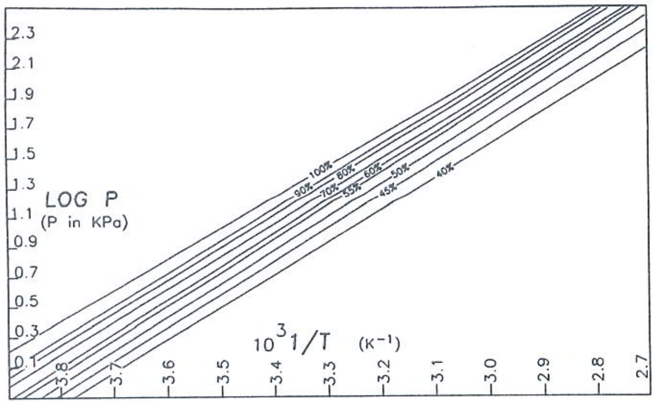

Fig.3 - P-T-X diagram of the mixture CH_3OH-LiBr-$ZnBr_2$ (1:2)

TABLE 1 - *Vapour Pressure of Methanol-Lithium Bromide-Zinc Bromide Systems*

X (%)	T (K)	P (KPa) 2:1	3:1	1:2
100	293.16	13.5	13.5	13.5
	303.16	21.9	21.9	21.9
	313.16	36.8	36.8	36.8
	343.16	129.1	129.1	129.1
	373.16	373.0	373.0	373.0
90	293.16	11.8	8.4	8.7
	303.16	20.3	19.1	18.8
	313.16	29.2	34.2	35.4
	323.16	52.8	54.6	54.3
	333.16	-	85.5	86.8
	343.16	125.0	125.3	127.0
	373.16	347.3	368.1	370.1
70	293.16	11.0	6.9	7.6
	303.16	19.3	13.2	16.7
	313.16	28.6	23.7	30.1
	323.16	46.3	39.7	51.0
	333.16	-	59.7	84.4
	343.16	102.6	87.4	123.5
	373.16	316.3	295.1	354.8
50	293.16	4.2	1.8	5.8
	303.16	9.3	6.1	12.6
	313.16	16.8	12.6	22.7
	323.16	27.5	21.9	38.2
	333.16	42.4	33.7	57.9
	343.16	62.5	49.5	86.2
	373.16	169.6	102.0	201.8
40	293.16	1.0	0.8	3.6
	303.16	3.9	3.2	8.5
	313.16	7.9	7.0	14.8
	323.16	13.3	11.7	24.8
	333.16	20.7	18.4	38.9
	343.16	29.7	26.9	57.5
	373.16	47.4	100.0	181.9

TABLE 2 - *CH_3OH-LiBr-$ZnBr_2$ (2:1) : Vapour Pressure Data. Comparison between Present Work, Iedema[6], Uemura[5]*

X (%)	T (K)	P (KPa) Present Work	Iedema	Uemura
90	303.16	19.4	21.0	19.8
	343.16	122.2	127.0	102.2
	373.16	379.1	368.0	-
70	303.16	18.4	18.5	14.6
	343.16	102.6	103.0	73.3
	373.16	304.4	307.6	-
50	303.16	9.5	9.8	-
	343.16	65.2	65.0	-
	373.16	194.4	195.0	-

of the curves is observed: increasing the molar ratio, the vapour pressure of the mixture also increases, for a fixed value of temperature and total weight concentration of salt. The experimental data for the ratio 2:1 are compared with data from Uemura-Hasaba [5] and Iedema [6]; a very good agreement is found with data from Iedema, while the comparison with data from Uemura- Hasaba is found less satisfactory (see tab. 2).

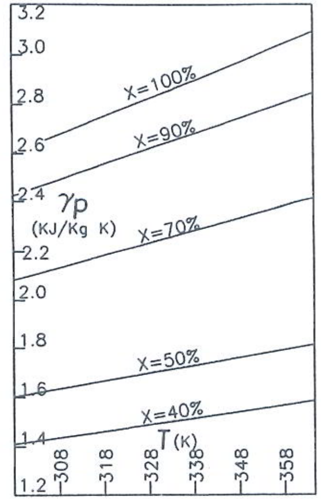

Fig.4 - CH_3OH-LiBr-$ZnBr_2$ (2:1) : Specific Heat vs. temperature for different concentrations

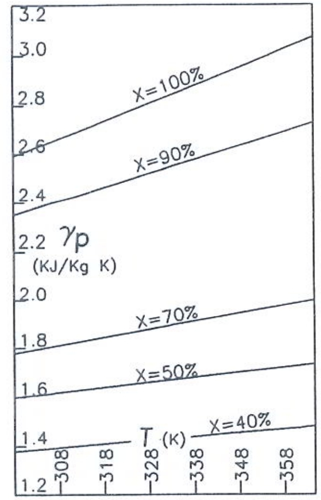

Fig.5 - CH_3OH-LiBr-$ZnBr_2$ (3:1) : Specific Heat vs. temperature for different concentrations

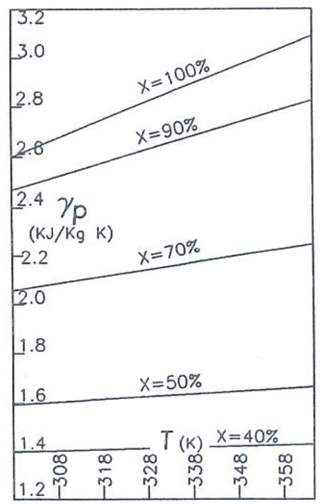

Fig.6 - CH_3OH-LiBr-$ZnBr_2$ (1:2) : Specific Heat vs. temperature for different concentrations

4. SPECIFIC HEAT

The specific heat is measured by a differential flux calorimeter (Calvet calorimeter, model Setaram C80). The characteristics of the instruments and the operating procedure were described in previous works [3], [4]. The direct experimental results consist of a great lot of data, so that they are not reported for sake of brevity; anyway they can be correlated by straight lines, so that the figg. 4, 5, 6 are sketched. It may be observed that the variation of the molar ratio between the two salts does not produce meaningful modifications on the values of the specific heats of the mixtures.

5. KINEMATIC VISCOSITY

The kinematic viscosity is measured by an Ubbelohde gravity viscosimeter, as it is described in previous

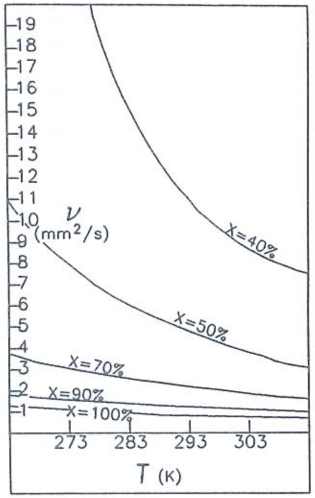

Fig.7 - CH_3OH-LiBr-$ZnBr_2$ (2:1) : Kinematic Viscosity vs. temperature for different concentrations

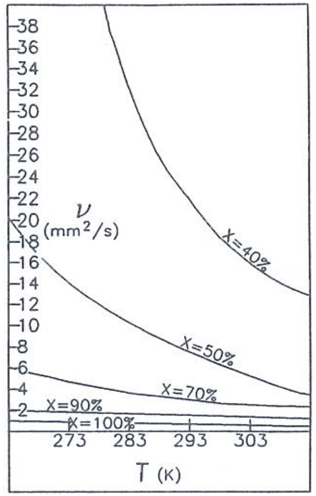

Fig.8 - CH_3OH-LiBr-$ZnBr_2$ (3:1) : Kinematic Viscosity vs. temperature for different concentrations

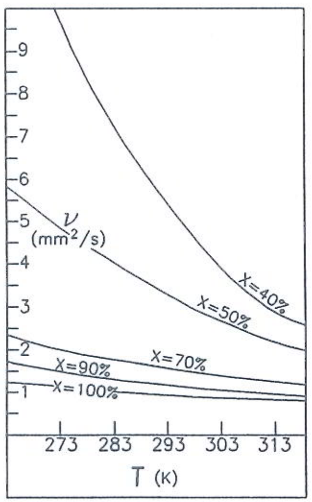

Fig.9 - CH_3OH-LiBr-$ZnBr_2$ (1:2) : Kinematic Viscosity vs. temperature for different concentrations

works [3], [4]. For each sample, at least six experimental determinations have been operated and the results are reported in table 3. The data can be interpolated with second degree lines and sketched on the figg. 7, 8, 9. When the molar ratio MR between the salts LiBr and $ZnBr_2$ decreases, the viscosity increases very rapidly; this fact was pointed out by Aker et Al. [7]. We have tried to put into evidence the entity of this phenomenon: on fig. 10 the values of the viscosity are reported vs. the molar ratio MR. Supplementary sets of measures have been carried on for the molar ratios 1:1 and 1:3, in order to better fit the experimental data. The viscosity of CH_3OH-LiBr is very high and it is included in the field 25 ÷ 100 mm^2/s, while the temperature varies in the range 10 ÷ 40 °C. Increasing MR, the viscosity rapidly decreases and for MR in the nearby of 0.66, it reaches the field 1.8 ÷ 4.0 mm^2/s, which is maintained, for the same range of temperatures, up to solutions CH_3OH-$ZnBr_2$ (MR = 1).

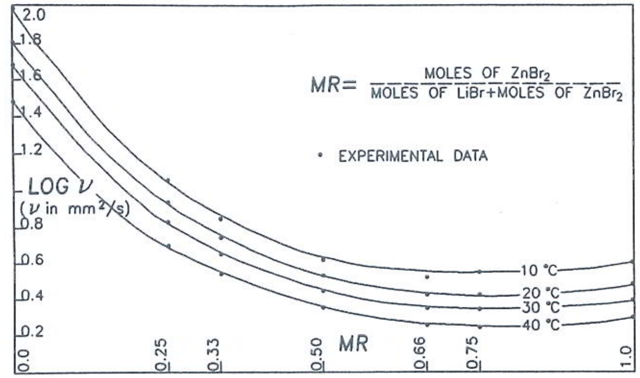

Fig.10 - Kinematic Viscosity vs. Molar Ratio between Lithium-Bromide and Zinc-Bromide, for different values of the temperatures

TABLE 3 - *Kinematic Viscosities of Metanol -Lithium Bromide-Zinc Bromide Systems*

X (%)	T (K)	ν (mm2/s) 2:1	3:1	1:2
	273.16	1.210	1.210	1.210
	283.06	1.120	1.120	1.120
100	296.46	0.999	0.999	0.999
	303.16	0.947	0.947	0.947
	313.16	0.913	0.913	0.913
	323.16	0.867	0.867	0.867
	263.16	1.787	1.972	1.640
	273.16	1.558	1.691	1.423
90	283.16	1.381	1.453	1.264
	293.16	1.214	1.287	1.148
	303.16	1.109	1.160	1.034
	313.16	1.050	1.084	0.954
	263.16	3.781	5.929	2.385
	273.16	3.011	4.634	1.885
70	282.16	2.538	3.747	1.603
	293.16	2.110	3.066	1.366
	303.16	1.819	2.579	1.209
	313.16	1.574	2.200	1.098
	263.16	10.472	20.343	5.708
	273.16	7.866	14.405	4.144
50	283.16	5.981	10.448	3.155
	293.16	4.784	8.129	2.534
	303.16	3.856	6.287	2.102
	313.16	3.157	5.093	1.811
	263.16	32.741	78.109	11.846
	273.16	22.252	48.631	7.763
40	283.16	16.074	31.934	5.524
	293.16	11.662	21.988	4.121
	303.16	8.927	15.642	3.214
	313.16	7.096	11.700	2.669

TABLE 4 - *Densities of Methanol-Lithium Bromide-Zinc Bromide Systems*

X (%)	T (K)	ρ (Kg/m3) 2:1	3:1	1:2
	263.16	818.8	818.8	818.8
	273.16	809.9	809.9	809.9
100	293.16	791.1	791.1	791.1
	313.16	772.1	772.1	772.1
	333.16	754.0	754.0	754.0
	263.16	-	898.1	894.6
	273.16	-	889.5	885.8
90	280.16	894.6	-	-
	293.16	891.1	870.8	867.9
	313.16	872.6	852.9	850.3
	333.16	854.1	834.9	832.9
	263.16	1123.6	1094.9	1124.3
	273.16	1115.3	1086.6	1116.6
70	293.16	1096.4	1068.4	1098.7
	313.16	1078.1	1050.3	1083.0
	333.16	1060.0	1033.8	1067.1
	263.16	1452.4	1377.9	1436.7
	273.16	1445.8	1370.4	1433.3
50	293.16	1428.5	1353.6	1418.3
	313.16	1410.9	1337.2	1401.6
	333.16	1393.0	1319.9	1386.0
	263.16	1686.0	1573.4	1562.2
	273.16	1676.1	1563.3	1556.0
40	293.16	1658.9	1550.2	1541.4
	313.16	1641.4	1532.8	1526.5
	333.16	1622.7	1515.9	1508.8

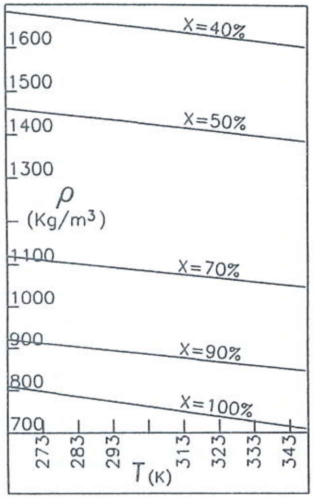

Fig.11 - CH_3OH-LiBr-$ZnBr_2$ (2:1) : Density vs. temperature for different concentrations

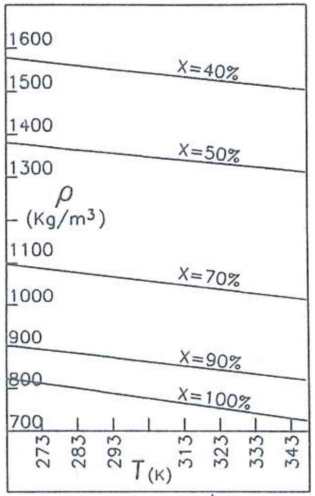

Fig.12 - CH_3OH-LiBr-$ZnBr_2$ (3:1) : Density vs. temperature for different concentrations

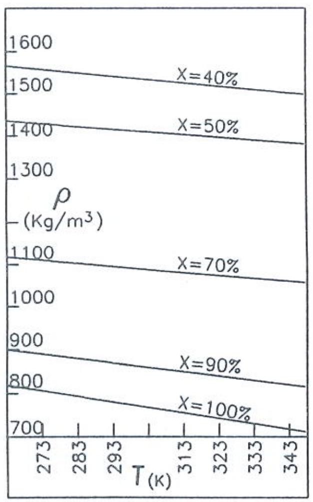

Fig.13 - CH_3OH-LiBr-$ZnBr_2$ (1:2) : Density vs. temperature for different concentrations

So, in order to avoid high value of the viscosity, a molar ratio higher than 0.5 should be considered.

6. DENSITY

The densities of the mixtures are measured by means of a glass vessel having a volume of 220 cm^3; the vessel has a graduated neck which allows to appreciate maximum variations of volume as high as about 20 cm^3, with a sensibility of about 0.1 cm^3. Before each measure the vessel is accurately cleaned and dried, then filled with the sample and closed up. After the vessel is put inside the climatic room; a magnetic stirrer is used to avoid stratification. At least four measures are made for each sample and the results are reported in table 4; they can be correlated by straight lines, which are sketched on figg. 11, 12, 13.

7. COMPARISON OF FLUIDS

The fluids are compared with each other supposing that they are employed within an absorption refrigerating machine; two evaporating temperatures are considered, the first one is equal to -10 °C (Cold Storage), the second one is equal to +3 °C (Air Conditioning). In the latter case, the mixture H_2O-LiBr is also included in the comparison; the data are taken from Mc Neely [9]. The temperature T_o of the environment is variable in the range 0 ÷ 35 °C.

Two types of analysis are carried on. In the first one (fig.14) the temperature T_h of the heating fluid is reported vs. T_o. The temperature T_h is supposed to be 10 °C higher than the minimum generator temperature for the given operating conditions [10]. The best performances are shown by CLZ31, which exhibits the lower T_h, both with T_e = -10 °C and T_e = +3 °C; CLZ31 is followed by CLZ21, while the curves of CLZ12 are early interrupted, because invading the crystallization zone. All fluids look better than H_2O-LiBr, at T_e = +3 °C; anyway the differences between the T_h of the different fluids do not exceed 5 °C. In the second analysis (fig.15) the theoretical C.O.P. is reported vs. T_o. The C.O.P. looks practically insensible to variations of the evaporating temperatures. A marked influence of the fluid nature may be observed: H_2O-LiBr is undoubtely the best mixture (only for T_e = +3 °C), while CLZ21 shows better performances than the other alcohol-salt ternary mixtures; this behaviour is enhanced at low environment temperatures. It may be concluded that, among the ternary mixtures CH_3OH-LiBr-$ZnBr_2$, the mixture named CLZ21 shows, in the whole, the most desirable set of characteristics for use in an absorption refrigerating machine.

8. LIST OF SYMBOLS

A = Constant in Antoine Equation
B = Constant in Antoine Equation (K)
CLZ21 = Ternary Mixture CH_3OH-LiBr-$ZnBr_2$ (2:1)
CLZ31 = Ternary Mixture CH_3OH-LiBr-$ZnBr_2$ (3:1)
CLZ12 = Ternary Mixture CH_3OH-LiBr-$ZnBr_2$ (1:2)
C.O.P. = Coefficient of Performance
MR = (Moles of $ZnBr_2$) / (Moles of LiBr + Moles of $ZnBr_2$)
P = Pressure (KPa)
T = Temperature (°C, K)
X = Concentration of Refrigerant (% by weight)

<u>Greek Letters</u>

γ = Specific Heat (KJ/Kg K)
ν = Kinematic Viscosity (mm^2/s)
ρ = Density (Kg/m^3)

<u>Subscripts</u>

e = evaporator
h = supply
o = environment

9. AKNOWLEDGEMENTS

This work has been performed with the contribution of C.N.R., P.F.Ed. (Progetto Finalizzato Edilizia); the Authors are indebted with Prof. Claudio Cerruti, Director of P.F.Ed. and with Arch. Roberto Vinci, Director of Sub-Project P.F.Ed. 3.

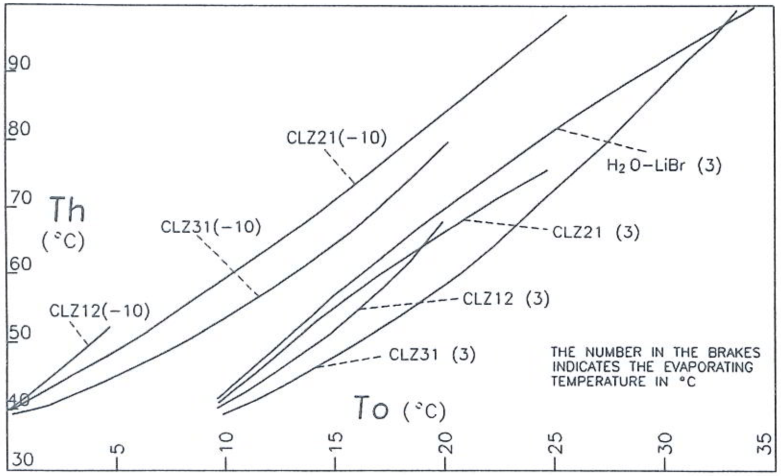

Fig.14 - T_h vs. T_o for the different mixtures. Curves are interrupted where the concentration of salt reaches the crystallization limit

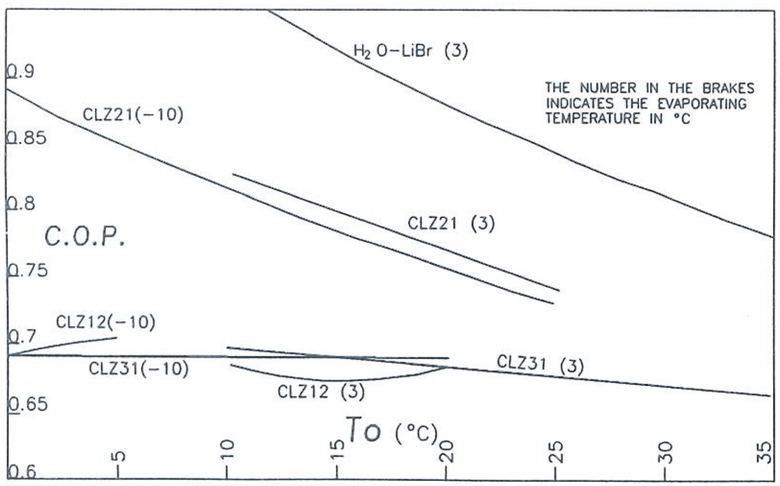

Fig.15 - C.O.P. vs. T_o for the different mixtures. Curves are interrupted where the concentration of salt reaches the crystallization limit

10. REFERENCES

[1] W.R. HAINSWORTH : "Refrigerants and Absorbents", Refrigeration Engineering, vol. 48, 1944, p. 97.

[2] S. IYOKI, T. TAKIGAWA, T. UEMURA : "Thermal and Physical Properties of the Methanol-Lithium Bromide-Zinc Chloride System", International Journal of Refrigeration, vol.14, March 1991.

[3] F. ASDRUBALI, C. BURATTI, F. COTANA, M. FELLI : "Alcune proprieta' termofisiche di soluzioni di Acqua e Xilitolo", Rapp. n. 2, C.N.R., P.F.Edilizia, Perugia 1991.

[4] M. FELLI, F. COTANA : "La nuova stazione di misura di proprieta' termofisiche dell'Istituto di Energetica dell'Universita' di Perugia", Rapp. n. 1, C.N.R., P.F.Edilizia, Perugia 1991.

[5] T. UEMURA, S. HASABA : "Studies on the Methanol-Lithium Bromide-Zinc Bromide Absorption Refrigerating Machine", Refrigeration (Japan), vol. 44, August 1969.

[6] P.D. IEDEMA : "The Absorption Heat Pump with Lithium Bromide-Zinc Bromide-Methanol", Delft University of Technology, 1984.

[7] J.E. AKER, R.G. SQUIRES, L.F. ALBRIGHT : "An Evaluation of Alcohol-Salt Mixtures as Absorption Refrigeration Solutions", ASHRAE J., May 1965, p. 90-92.

[8] E. GROSMAN, N.K. SUSLOVA, D.M. CHALAYEV : "Methanol as a Working Medium in Sorption Type Thermal Converters", XVI I.I.F. Congress, Paris, 1983.

[9] L.A. Mc NEELY: "Thermodynamic Properties of Aqueous Solutions of Lithium-Bromide", ASHRAE Transactions, n.3, 1979, p.413-434.

[10] M. FELLI : "Proprieta' termodinamiche di sistemi bifase a due componenti utilizzabili in macchine frigorifere ad assorbimento", Il Freddo, vol. 33, 1979.

[11]R.H. PERRY, D. GREEN : "Perry's Chemical Engineers Handbook", Sixth Edition, Mc Graw Hill, 1984.

[12]G. MONCADA LO GIUDICE et Al. : "Nuovi fluidi per trasformatori di calore", C.N.R., P.F.Energetica, RF 87.02729.59, 1990.

FLUIDES POUR ABSORPTION: DONNÉES EXPÉRIMENTALES ET PERFORMANCES OPERATIONELLES

Résumé : Le données expérimentales des propriétés thermophysiques sont determinées pour le composé ternaire CH_3OH-LiBr-$ZnBr_2$; plusieurs rapports molaires entre $ZnBr_2$ et LiBr sont examinés. Les performances des solutions quand ils travaillent dans un réfrigérateur à absorption sont calculées et comparées entre eux et aussi avec la solution H_2O-LiBr.