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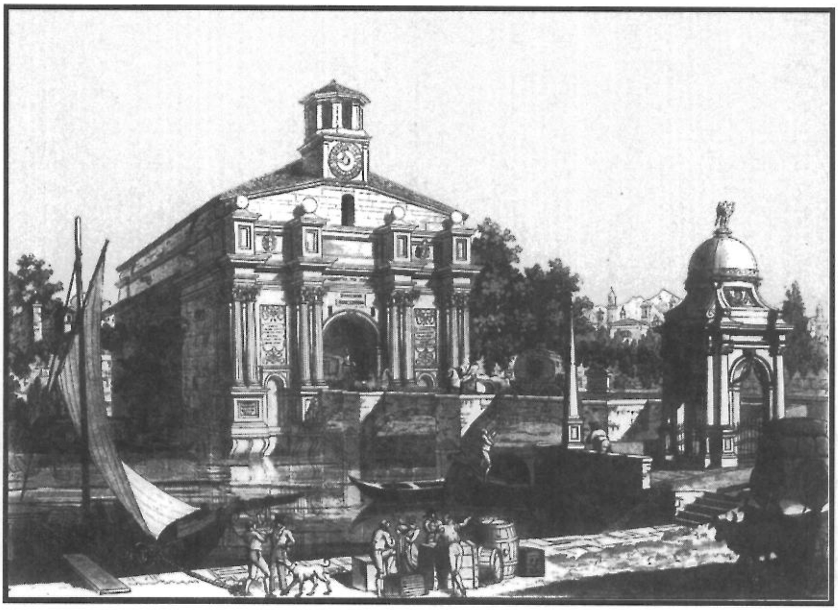

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THERMOPHYSICAL PROPERTIES OF H_2O-NaOH-KOH MIXTURES: EXPERIMENTAL DATA

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ABSTRACT

Sodium Hydroxide-Water mixtures were proposed for use in Absorption Refrigeration since one hundred years ago, because of their favourable vapour pressure characteristics. Unfortunately, they could not have commercial applications for their chemical aggressivity against most of suitable materials. In the recent years, progresses in the materials technology have made feasible the utilization of these compounds, so that several studies and also design patents have been developed. Usually ternary and quaternary mixtures are utilized, in order to increase solubilities and to have low viscosities.

In the present paper a ternary mixture H_2O-NaOH-KOH is considered, with different values of the mole ratio between salts. Vapour pressures, specific heats, kinematic viscosities and densities are experimentally determined. P-T-X diagrams are traced and mixtures with most favourable ratios between salts are selected.

INTRODUCTION

Water-Hydroxide mixtures present favourable characteristics for use in absorption applications, such as low solution specific volumes and high latent heats [1], [2]. Thermodynamic properties of H_2O-NaOH are even better than H_2O-LiBr, but solubilities and viscosities are far from desirable values [1]. On the contrary, the H_2O-KOH mixture exhibits high solubilities, low viscosities, but the thermodynamic properties are less valuable.

So, in the present paper, the ternary mixture H_2O-NaOH-KOH is examined, in order to verify if it is possible, with the use of an appropriate mole ratio between salts, to get a fluid which can be preferred, on the whole, to the classical pair H_2O-LiBr. The quaternary mixture containing CsOH, often proposed in the Literature [3], [4], [5], has been excluded because of the very high cost of this component (1$ per gram), which might have a meaningful incidence over the costs of the engine.

The following properties have been experimentally determined: vapour pressures, specific heats, densities, kinematic viscosities; all measures have been performed at different temperatures, pressures and concentrations, covering the application ranges of refrigerating machines, heat pumps, heat transformers.

DETERMINING OF THE MOLE RATIOS BETWEEN SALTS

The most appropriate mole ratios between salts have been evaluated by the following preliminary tests:

Vapour Pressure Test. A solution with a concentration of 70% of Water has been considered; the 30% Salt concentration is composed of variable mole ratio between KOH and NaOH. Vapour pressure measurements have been performed at constant temperature T=50°C, constant mass of water and variable salt ratio: the results are shown in fig. 1. It may be observed that the lowest vapour pressure is presented by the mixture 4:1 (that means four moles of NaOH for one mole of KOH).

Viscosity Test. The same fluids as above have been considered, but at a temperature of 20°C. The results are shown in fig. 2. The lowest value corresponds to pure KOH in solution. However, for KOH content higher than 1:2, the variation of viscosity is very limited. So this value has been considered as the lowest acceptable one for viscosity problems.

Solubility Test. Solubility tests at ambient temperature have been executed; the results are shown in fig. 3, where it may be noted that the solubilities increase up to the ratio 1:1, and after it remains practically constant.

Therefore, the following mixtures have been selected for experimental determinations:

A) Mole ratio 4:1;

B) Mole ratio 1:2;

C) Mole ratio 1:1.

To prepare the mixtures the same substances and procedures have been utilized as described in [1].

VAPOUR PRESSURE MEASUREMENTS

The experimental facility was described in previous papers [1], [6], [7], [8], [9], [10]: concentration is maintained constant, while temperature and pressure are varied and contemporary measured. For each concentration, at least four experimental points have been determined and after correlated by the Antoine equation:

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

Experimental results are shown in table. 1; the corresponding P-T-X charts, obtained by application of (1), are traced in fig. 4a, 4b, 4c.

The P-T-X charts of these ternary mixtures exhibit straight lines diverging at high temperatures, that is favourable for use in heat transformers. Among the examined ones, the mixtures with ratio 4:1 and 1:2 show better thermodynamic performances in heat transformers applications.

The solubility line has been determined following the method described in [6], [11]. A complete solubility in the tested ranges of P-T-X has been found, with the exception of the crystallization point in fig. 4a.

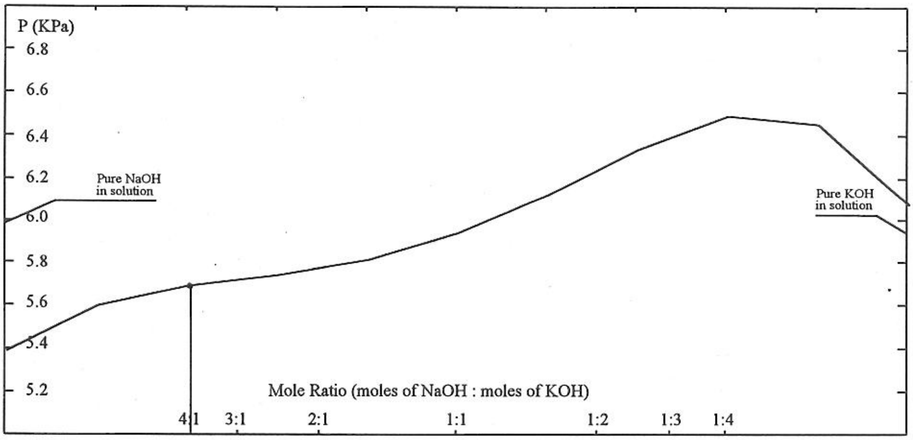

Fig. 1: Vapour Pressures of H_2O-NaOH-KOH solutions vs mole ratio between Salts (T=50°C, X=70% by mass of H_2O).

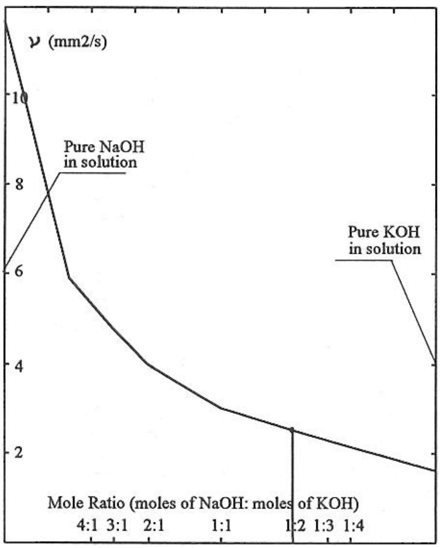

Fig. 2: Kinematic Viscosities of H_2O-NaOH-KOH solutions vs mole ratio between Salts (T=20°C, X=70% by mass of H_2O).

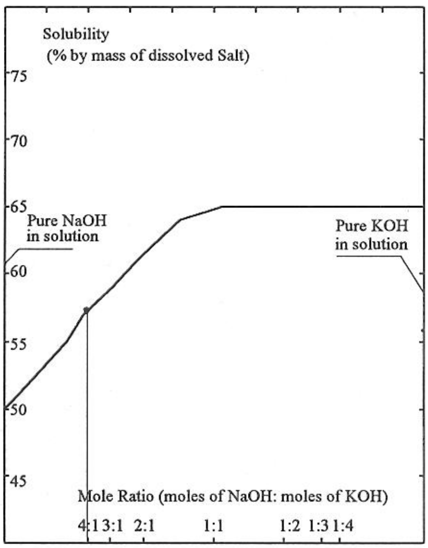

Fig. 3: Solubilities of H_2O-NaOH-KOH solutions vs mole ratio between Salts, at ambient temperature.

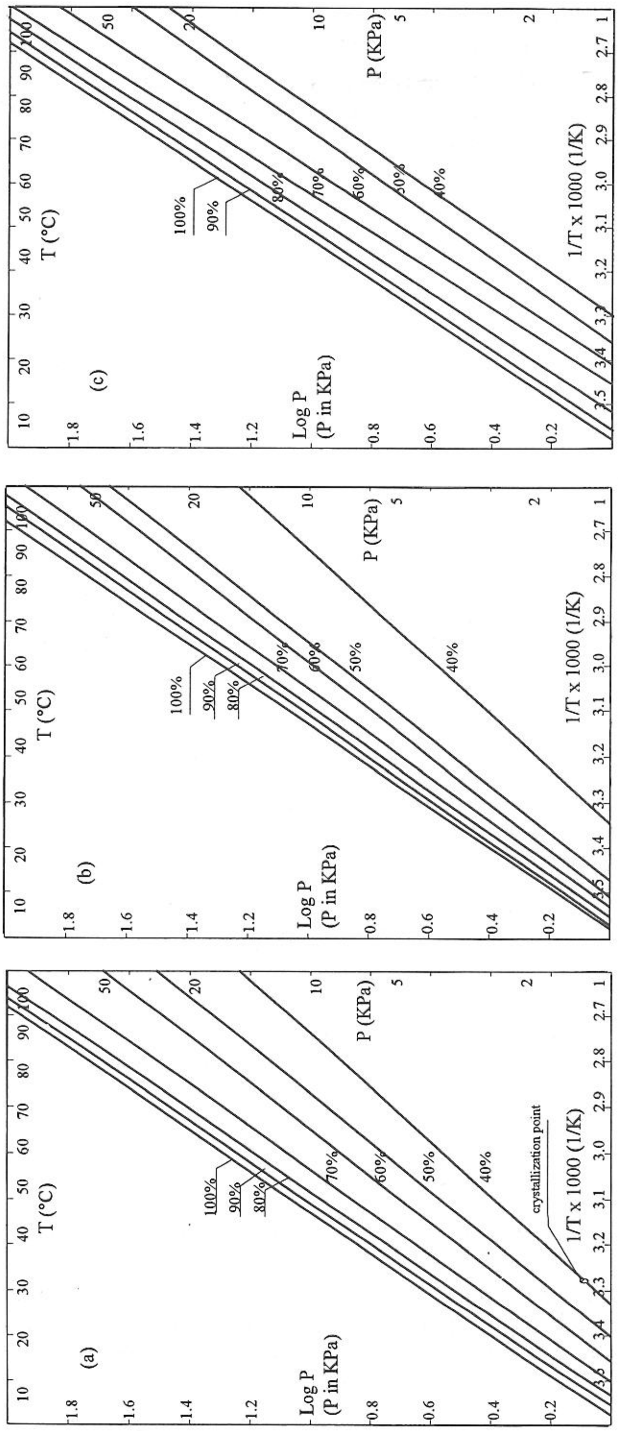

Fig. 4: *P-T-X diagrams of H_2O-NaOH-KOH solutions, with the following mole ratios between Salts: 4:1 (a), 1:2 (b), 1:1 (c).*

Tab. 1: *Vapour Pressures of H_2O-NaOH-KOH solutions vs temperature and concentration.*

X (%)	T (°C)	P (KPa)			X (%)	T (°C)	P (KPa)		
		4:1	**1:2**	**1:1**			**4:1**	**1:2**	**1:1**
100	30	4.25	4.25	4.25	60	30	-	2.75	1.58
	40	7.38	7.38	7.38		40	3.59	4.04	3.26
	50	12.34	12.34	12.34		50	4.99	5.97	5.69
	60	19.93	19.93	19.93		60	7.50	9.11	9.20
	70	31.18	31.18	31.18		70	11.73	14.28	14.70
	80	47.38	47.38	47.38		80	18.16	22.32	18.70
90	30	3.77	3.97	3.76	50	30	-	-	1.39
	40	6.53	6.53	6.77		40	-	3.66	2.30
	50	10.93	10.93	10.76		50	3.90	5.06	3.45
	60	17.92	16.76	17.74		60	5.65	7.33	5.62
	70	28.40	27.39	28.51		70	8.34	12.68	8.94
	80	43.67	42.87	-		75	10.05	-	-
	90	-	-	64.43		80	12.08	-	13.97
80	30	-	3.73	3.07	40	40	1.77	-	-
	40	5.76	6.25	5.69		50	2.47	2.89	2.40
	50	9.71	10.06	9.53		60	3.55	3.55	3.21
	60	15.79	16.21	15.68		70	5.09	4.85	6.52
	70	24.77	25.64	24.94		75	6.14	-	-
	80	37.94	39.37	38.43		80	7.50	7.36	9.60
70	25	1.98	-	-		85	8.48	-	-
	30	2.82	3.42	-					
	40	5.20	4.60	-					
	50	5.59	7.75	5.84					
	60	13.48	12.75	11.45					
	70	19.87	20.29	18.55					
	80	30.71	31.37	29.91					

SPECIFIC HEAT MEASUREMENTS

Specific heat measurements have been performed by differential thermal flux calorimeter (Calvet Calorimeter, mod. Setaram C80), as described in previous papers [8], [9], [10]. The results have been correlated by straight lines, as shown in the figures 5a, 5b, 5c. From this point of view, there are no meaningful differences among the three mixtures.

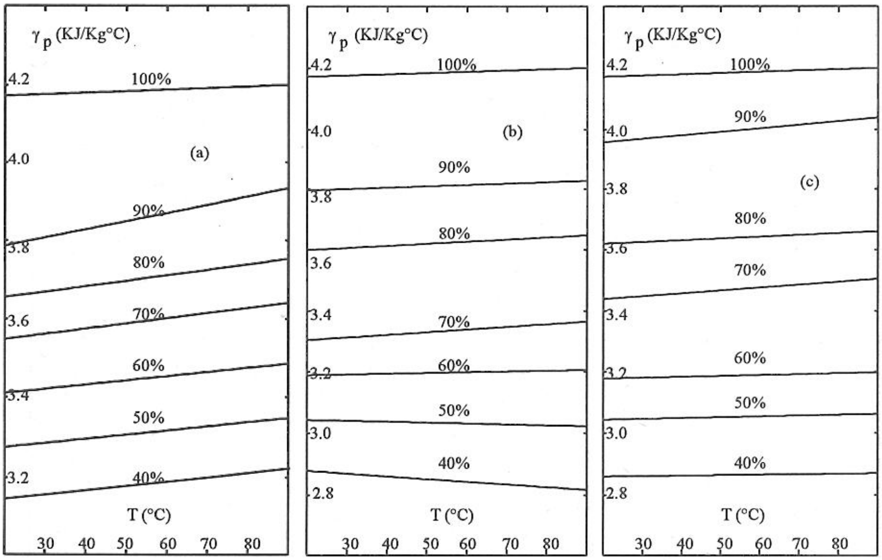

Fig. 5: Specific Heats of H_2O-NaOH-KOH solutions, with the following mole ratios between Salts: 4:1 (a), 1:2 (b) and 1:1 (c).

DENSITY MEASUREMENTS

Densities have been determined by a volumetric flask, following a procedure described in previous papers [1], [6], [7]. For each sample at least six experimental points have been determined, whose values are reported in table 2. The regression lines are traced in fig. 6a, 6b, 6c. The mole ratio between salts is not at all influencing the mixture densities and, by this way, all examined mixtures have favourable characteristics.

KINEMATIC VISCOSITY MEASUREMENTS

Kinematic viscosity measurements have been carried on by Ubbelhode viscometers, as in previous works [1], [6], [7], [8], [9], [10].

For each sample, at least five experimental points have been determined and results are shown in table 3; the interpolating lines are traced in fig. 7a, 7b, 7c.

The mixture 1:2 looks the best one, having the lowest viscosity values. However, in a wide range of the salt ratio, the viscosities are in the same range as that of the H_2O-LiBr mixtures.

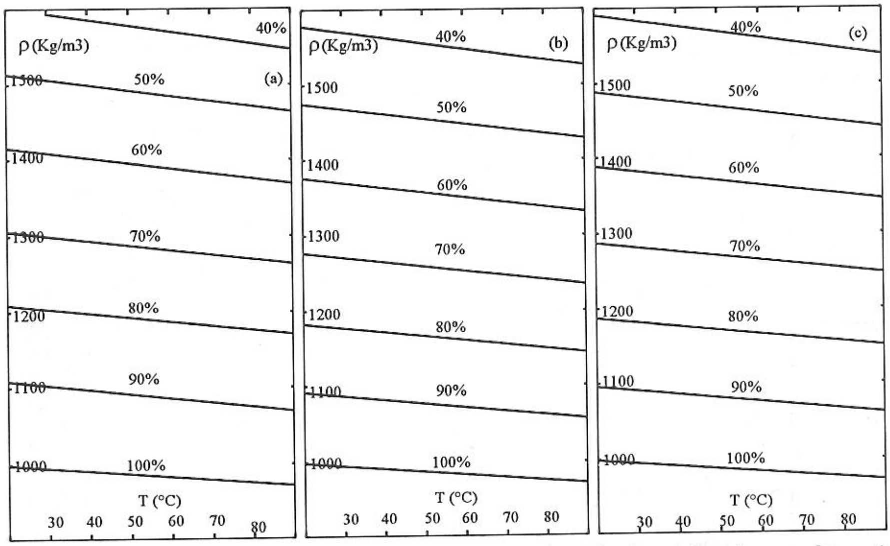

Fig. 6: *Densities of H_2O-NaOH-KOH solutions, with the following mole ratios between Salts: 4:1 (a), 1:2 (b) and 1:1 (c).*

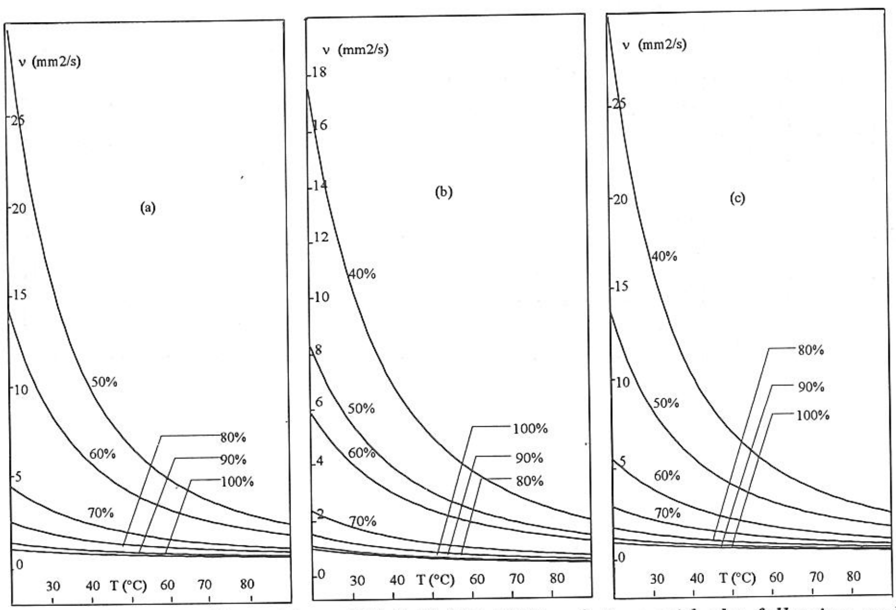

Fig. 7: *Kinematic Viscosities of H_2O-NaOH-KOH solutions with the following mole ratios between Salts: 4:1 (a), 1:2 (b) and 1:1 (c).*

Tab. 2: Densities of H_2O-NaOH-KOH solutions vs temperature and concentration.

X (%)	T (°C)	ρ (Kg/m^3)			X (%)	T (°C)	ρ (Kg/m^3)		
		4:1	1:2	1:1			4:1	1:2	1:1
100	10	1000.6	1000.6	1000.6	60	10	-	-	1394.4
	20	999.1	999.1	999.1		20	1415.0	1352.7	1388.8
	30	996.6	996.6	996.6		30	1409.4	1370.0	1382.6
	40	992.5	992.5	992.5		40	1402.4	1362.6	1375.8
	50	987.7	987.7	987.7		50	1395.8	1356.4	1370.0
	60	983.4	983.4	983.4		60	1388.6	1350.1	1363.0
	70	977.4	977.4	977.4		70	1381.8	1343.6	1357.0
90	10	-	1095.5	1099.3		80	-	1337.2	1350.4
	20	-	1091.7	1095.8	50	10	-	-	1496.6
	30	1102.7	1087.9	1091.5		20	1514.3	1471.5	1489.2
	40	1097.8	1083.1	1087.2		30	1506.9	1468.6	1481.9
	50	1092.4	1078.3	1081.9		40	1500.3	1461.4	1475.3
	60	1086.8	1073.0	1076.7		50	1493.0	1455.0	1468.1
	70	1080.7	1067.8	1070.5		60	1485.8	1448.6	1461.7
	80	1074.9	1059.6	1064.3		70	1478.6	1441.7	1454.6
80	10	-	-	1192.2		80	-	1434.7	1448.3
	20	1208.8	1180.8	1187.3	40	10		-	1599.4
	30	1204.6	1177.4	1182.1		20	-	-	1590.6
	40	1199.2	1172.1	1177.0		30	-	1568.6	1583.1
	50	1193.9	1166.4	1171.6		40	-	1565.5	1575.7
	60	1187.4	1161.0	1165.7		50	-	1554.7	1568.0
	70	1181.0	1155.4	1160.4		60	-	1551.6	1561.1
	80	-	1149.5	1154.1		70	-	1540.2	1553.5
70	10	-	-	1292.8		80	-	1532.7	1546.0
	20	1305.6	-	1287.1					
	30	1300.4	1271.2	1282.0					
	40	1294.7	1265.3	1276.4					
	50	1288.1	1259.4	1270.8					
	60	1281.6	1253.3	1264.7					
	70	1275.7	1247.3	1258.7					
	80	-	1241.3	1252.1					

Tab. 3: Kinematic Viscosities of H_2O-NaOH-KOH solutions vs temperature and concentration.

X (%)	T (°C)	ν (mm²/s)			X (%)	T (°C)	ν (mm²/s)		
		4:1	1:2	1:1			4:1	1:2	1:1
100	10	1.28	1.28	1.28	60	10	-	-	8.45
	20	1.02	1.02	1.02		20	-	3.97	5.58
	30	0.83	0.83	0.83		30	8.49	3.00	-
	40	0.71	0.71	0.71		40	5.72	2.36	2.89
	50	0.62	0.62	0.62		50	4.07	1.93	2.24
	60	0.56	0.56	0.56		60	3.09	1.62	1.81
	70	0.51	0.51	0.51		70	2.44	1.41	1.49
	80	0.47	0.47	0.47		80	2.00	-	1.26
90	10	-	-	1.60	50	10	-	-	23.57
	20	-	1.31	1.27		20	-	8.13	15.12
	30	1.10	0.91	1.04		30	16.14	5.67	8.33
	40	0.91	0.77	0.87		40	9.90	3.91	5.62
	50	0.79	0.67	0.76		50	6.61	2.99	4.10
	60	0.69	0.60	0.67		60	4.73	2.38	3.16
	70	0.61	0.55	0.60		70	3.55	1.96	2.50
	80	0.56	-	0.55		80	2.80	-	2.06
80	10	-	-	2.38	40	10	-	-	64.24
	20	-	-	1.82		20	-	17.45	29.94
	30	1.87	1.21	1.45		30	-	10.67	16.78
	40	1.47	1.00	1.18		40	-	7.01	10.28
	50	1.21	0.85	1.00		50	-	5.01	7.05
	60	1.04	0.75	0.87		60	-	3.75	5.15
	70	0.89	0.67	0.77		70	-	2.95	3.85
	80	0.79	0.61	0.68		80	-	-	3.07
70	10	-	-	4.11					
	20	-	-	2.97					
	30	3.18	1.79	2.24					
	40	2.38	1.43	1.77					
	50	1.86	1.18	1.44					
	60	1.51	1.01	1.21					
	70	1.25	0.88	1.04					
	80	1.06	0.78	0.91					

ERRORS

A detailed discussion of errors is made in [7], [8], [9]. However, for sake of completeness, a synthesis is shown in table 4.

Tab. 4: Measurement errors.

MEASUREMENT	MAXIMUM ABSOLUTE ERROR	
P-T-X	pressure	$\pm 3 \times 100$ Pa
	concentration	$\pm 4 \times 0.001$ Kg
	temperature	± 0.05 K
SPECIFIC HEAT	± 0.0361 KJ/KgK	
DENSITY	± 0.63 Kg/m^3	
KINEMATIC VISCOSITY	$\pm 0.02 \times 10^{-6}$ m^2/s	

CONCLUSIONS

The thermophysical properties of the thernary mixtures H_2O-NaOH-KOH have been experimentally determined, with mole ratio between salts equal to 4:1, 1:2, 1:1.

The best compromise among the values of the different properties, in order to be used in absorption units, is shown by the mixture having ratio 1:2. This one, if introduced in a heat transformer supplied at 40°C, exhibits better performances than H_2O-LiBr (15% higher temperatures at the absorber), as a consequence of diverging of P-T-X lines at high temperatures.

Viscosity values are low; corrosion is avoided by use of Chromates as inhibitors and the engine is built up with a Cupro-Nichel alloy. Therefore the mixture can be proposed for use in heat transformers.

NOMENCLATURE

A = constant in Antoine's equation;
B = constant in Antoine's equation (K);
P = pressure (KPa);
T = temperature (K, °C);
X = refrigerant mass fraction.

Greek Letters

γ = specific heat (KJ/KgK);
ν = kinematic viscosity (mm^2/s);
ρ = density (Kg/m^3).

Subscripts

p = at constant pressure;

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