Vapor-Liquid Equilibria of aqueous alkaline nitrate and nitrite solutions for Absorption Refrigeration Cycles with High Temperature Driving Heat

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Vapor-liquid equilibria of aqueous solutions of lithium nitrate + potassium nitrate + sodium nitrate in the mass ratio (53:28:19) and lithium nitrate + potassium nitrate + sodium nitrite in mass ratio (53:35:12) were obtained using a static method in the temperature range 333.15 K to 473.15 K at 20 K intervals. Both mixtures were considered as binary working fluids (water/salts). The salt mass fraction was varied from 0.50 to 0.95. Barker's method was used to calculate the liquid composition from the initial overall composition of the sample and the measured pressure and temperature. The vapor-liquid equilibria data obtained were correlated using an analytical polynomial equation. The calculated and measured data showed good agreement. The vapor-liquid equilibria data of both mixtures showed similar behaviour, but the risk of crystallization is lower for the solution of lithium nitrate + potassium nitrate + sodium nitrite in mass ratio (53:35:12), which favours the operation of absorption refrigeration cycles driven by high temperature heat sources.

Key words: vapor-liquid equilibrium, aqueous alkaline nitrate and nitrite solutions, absorption refrigeration cycles.

Introduction

Current technological developments in thermal cooling systems driven by high temperature heat sources focus on direct-fired double-effect absorption chillers. However, these chillers do not perform sufficiently well to compete with centrifugal chillers. Conventional water-lithium bromide double-effect direct-fired absorption chillers, which have a cycle cooling coefficients of performance (COPs) of around 1.2, do not use the temperature level of the driving heat because of corrosion and thermal stability problems associated with the working pair at temperatures over 423.15 K.

Triple effect absorption cooling systems can improve COP by up to 50% compared with the conventional double-effect cooling systems (Erickson[1]). However, triple effect cycles require new and unusual operating conditions in terms of temperature (over 423.15 K), solubility fields, and pressure. The corrosion additives conventionally used in LiBr solution are not effective at the high temperatures required by triple effect cycles.

To improve the cooling cycle performance, it is necessary to use advanced cycle configurations and/or new working pairs that take advantage of the temperature level of the driving heat. Davidson and Erickson[2] proposed using aqueous solutions of three alkali-metal nitrate salts - namely, lithium nitrate ($LiNO_3$), potassium nitrate (KNO_3) and sodium nitrate ($NaNO_3$), - to extend the upper temperature limit of absorption systems to 533.15 K or above. This contrasts with the limit of about 423.15 K for H_2O/LiBr, which is caused by problems of thermal stability and corrosion. The relative weight percent of the salts in the absorbent was ($LiNO_3$ + KNO_3 + $NaNO_3$) (53:28:19) (Davidson and Erickson[2]). Lithium nitrate was the main component because of its high specific heat and absorbing capacity. Davidson and Erickson[3] published experimental data of vapor pressure for this working pair in a temperature range from 313.15 K to 473.15 K and a salt mass fraction range from 0.50 to 0.94. Afterwards, Ally[4] fitted these data to a polynomial correlation in a salt mass fraction between 0.70 and

0.94 and with temperatures up to 533.15 K. He also used this new working pair to carry out simulation work in an absorption heat transformer and concluded that this absorption cycle shows greater efficiency, temperature lift and absorption potential than the conventional working pair H_2O/LiBr. Erickson and Howe[5] carried out further research into this new working fluid called "Alkitrate". They carried out various tests on corrodibility, thermal stability, performance and heat and mass transfer under typical absorption cycle operating conditions. They concluded that this working pair is suitable for high temperature absorption cycles (up to 530.15 K). Also, Alkitrate would have a potentially significant cost advantage due to the lower cost of the absorbent itself (Erickson and Howe[5]). However, Alkitrate is of limited use at low temperatures and pressures because its range of solubility is narrow and because the working concentration of alkaline-metal nitrate salts cannot be cooled to the ambient temperature, which results in crystallization problems. For this reason, Erickson[1] recommended that this working pair be used only in the high temperature components of the absorption system.

Vargas et al.[6] conducted an experimental study on the solubility of 21 Alkitrate samples, including Davidson and Erickson's working pair. The working pair H_2O-($LiNO_3$ + KNO_3 + $NaNO_2$) with a relative absorbent weight percent of (53:35:12) showed the highest solubility.

Álvarez[7] used the working pairs of Davidson and Erickson[2] and Vargas et al.[6] in a simulation study with a triple-effect absorption cycle. This consisted of a water-lithium bromide double-effect cycle coupled with a higher single-effect cycle that used Alkitrate as the working pair. The vapor pressure data required for this kind of simulation was predicted using the E-NRTL thermodynamic model developed by Álvarez[8].

In this study, we carried out vapor pressure measurements of the two Alkitrate working pairs using a static method between 333.15 and 473.15 K at 20 K intervals and varying the salt weight percent from 50 to 95%. Barker's method was used to calculate the liquid composition at equilibrium from the total initial composition and temperature data for both working pairs. The equilibrium data were then fitted using a polynomial equation. Also, experimental and calculated data obtained for Davidson and Erickson's working pair were compared with the values predicted by Ally's correlation[4].

The VLE data as well as the solubility curves obtained in the present work for aqueous alkaline nitrate and nitrite solutions are necessary for assessing by numerical simulation the performance and operating conditions of the multiple-effect absorption cooling cycles using these working fluids.

Experimental section

Materials. The salts used were $LiNO_3$ (Fluka, 99%), KNO_3 (Panreac, 99%), $NaNO_3$ (Panreac, 99%), $NaNO_2$ (Aldrich, 99%). The salts were all dried in a vacuum furnace at 393.15 K for a couple of days. All solutions were prepared using Millipore water (resistivity lower than 18.2 MΩ). The solutions were then carefully weighed using a Mettler electronic balance with a resolution of 1.0 mg to obtain the desired concentration.

Apparatus and experimental procedure. The vapor pressure of the aqueous alkaline nitrate and nitrite solutions was measured using a static method. The experimental procedure and equipment were previously described in Esteve[9]. The experimental equipment, which is schematically shown in Figure 1, consists of an equilibrium cell, a differential pressure null transducer (DPT, Ruska model 2439-702), a differential pressure null indicator (Ruska model 2416-711), a pressure controller (Ruska model 3891-801), and a double walled thermostated bath filled with oil. A Haake proportional temperature controller was used to control the temperature of the oil thermostat in a range between 333.15 and 473.15 K. The accuracy of the temperature controllers was ± 0.01 K. The temperature was measured very near the cell using a platinum resistance thermometer MKT 100 (Anton Paar). The pressure was measured by a digital pressure gauge (Ruska Model 6242) with two ranges of 0-150 kPa and 0-1000 kPa with a resolution of ± 0.001 kPa. The experimental uncertainty was evaluated in accordance with the NIST Technical guidelines regarding the expression of uncertainty in measurement (Taylor and Kuyatt[10]).

The first step in preparing the alkaline nitrate and nitrite solutions was to fill the equilibrium cell with the ternary salt. Davidson and Erickson's ternary salt consists of the following components: $LiNO_3$, KNO_3 and $NaNO_3$ (53:28:19, weight percent), whereas Vargas et al.[6] propose the following mixture:

$LiNO_3$, KNO_3 and $NaNO_2$ (53:35:12, weight percent). Second, the corresponding amount of water was added and the equilibrium cell was connected to the differential pressure null transducer. Both working mixtures were prepared at eight different total salt mass fractions: that is, 0.50, 0.60, 0.70, 0.75, 0.80, 0.85, 0.90 and 0.95. The sample in the cell, was continuously stirred by a magnetic needle driven from outside via magnetic coupling by a variable speed electric motor. Then, the sample filling the equilibrium cell was frozen using liquid nitrogen, and the incondensable gases were extracted from the equilibrium cell with a vacuum pump.

After this, the cell and lower part of the DPT were introduced to the bath. The vapor pressure of the sample was balanced by applying nitrogen gas to the top of the DPT and adjusting the pressure with the pressure controller to give a zero null indication. The vapor pressure of the sample was first measured at 333.15 K. After equilibrium was reached the pressure was measured by a digital gauge. Then the temperature was raised successively from 333.15 K to 473.15 K at 20 K intervals.

The methodology adopted was previously validated for pure water. Vapor pressure was measured for water in a temperature range between 323.15 K and 413.15 K at intervals of 20 K. The experimental results were compared with data reported by Wagner and Pruss[11]. The maximum deviation obtained was about 1.07% and the relative root mean square deviation (RMSD) was around 0.51%. These results validate our experimental procedure.

Modeling of the vapor–liquid equilibrium

The calculation procedure for determining the equilibrium composition from the initial composition of the samples and the measured vapor pressure and temperature for nitrate and nitrite ternary mixtures + water in an equilibrium state was the same as that described by Herraiz[12] the binary system. To obtain accurate vapor-liquid equilibrium p, x, T data, we applied Barker's method[13]. In this approach, an expression for the excess Gibbs free energy (G^E) of the liquid phase (equation 1) was assumed and parameters in this expression were obtained by fitting *P, x* data at each temperature. An orthogonal *n* degree polynomial Redlich-Kister form was used for the G^E model in this work

$$\frac{G^E}{x_1 x_2 RT} = A_1 + A_2(2x_1 - 1) + A_3(2x_1 - 1)^2 + \ldots + A_n(2x_1 - 1)^{n-1} \tag{1}$$

where x_1 is the salt mole fraction in the liquid and x_2 the corresponding water mole fraction.

The data fitting was performed using a Marquardt nonlinear regression program that minimizes the following objective function:

$$OF = \sum_i^N \left[\frac{\left(p^{calc} - p^{\exp}\right)_i}{p_i^{\exp}} \right]^2 \tag{2}$$

where N is the number of experimental data, and $p^{\exp}$ and p^{calc} are the experimental and calculated values, respectively, at a given temperature.

The corrections from overall input cell composition to actual liquid-phase composition at equilibrium conditions were performed for each temperature. In this procedure, the nonideal behavior of the vapor-phase was taken into account by using the virial equation of state truncated at the second virial coefficient. In this vapor phase, only the presence of water was considered, for which the second Virial coefficient from Rumpf and Maurer[14] were used. Moreover, we used the critical properties, acentric factor and equations of Saul and Wagner[15] for the vapor pressure and density of pure water.

Results and discussion

The vapor pressure of two aqueous alkaline nitrate and nitrite solutions was measured using a static method in the temperature range 333.15-473.15 K at 20 K intervals and varying the total salt mass fraction from 0.50 to 0.95.

The experimental vapor-pressure data and estimated liquid-phase composition results for aqueous alkaline nitrate and nitrite solution are reported in Table 1 for both selected working pairs.

The experimental values of pressure (p/kPa), temperature (T/K) and liquid-phase mass fraction were fitted to an analytical polynomial equation (3):

$$\ln(p/\mathrm{kPa}) = \sum_{i=0}^{2} a_i w^i + \frac{\sum_{i=0}^{2} b_i w^i}{T/\mathrm{K}} \tag{3}$$

where w is the liquid-phase mass fraction and the parameters a_i and b_i were determined from the experimental vapor pressure data by the least-squares method. These parameters are reported in Table 2.

The relative root-mean-square deviation (RMSD) was about 1.09% for Davidson and Erickson's working pair[2], whereas the RMSD was 1.11% for the working pair of Vargas et al.[6]. The relative RMSD was calculated using equation (4):

$$RMSD = 100\left[\frac{1}{N}\sum_{i=1}^{N}\left(\frac{p^{\exp} - p^{calc}}{p^{\exp}}\right)_i^2\right]^{1/2} \tag{4}$$

where N is the number of experimental data, and p^{exp} and p^{calc} are the experimental and calculated values, respectively. The maximum relative deviation between experimental and calculated data was 3.99% for Davidson and Erickson's working pair[2] and 2.58% for the working pair of Vargas et al.[6]

Plots of ln$p$ versus -1000/T (Figures 2 and 3) show a linear behavior, and that pressure increases with temperature and salt composition. Figures 2 and 3 illustrate the experimental data obtained with the working pairs proposed by Davidson and Erickson, and Vargas et al., respectively. They also show the deviations between the experimental data and the calculated values using polynomial correlation at different temperatures and salt concentrations and that there is good agreement between these.

The crystallization temperature reported by Vargas et al.[6] for both working pairs was also plotted (see Figure 3). A simple comparison of the two crystallization curves shows that the crystallization temperature line of Davidson and Erickson's working pair is always above that of the working pair of Vargas et al. The difference in crystallization temperature between the two working pairs varies approximately between 16 K and 26 K, which makes possible the operation of the generator connected to the heat source at higher temperatures.

In Figure 4 the experimental vapor pressure data are compared with the calculated values by the analytical polynomial equation from the present study, and numerical values calculated from the correlation proposed by Ally[4] for vapor pressure versus solution temperature at salt mass fractions between 0.70 and 0.95 for Davidson and Erickson's working pair[2]. It can be observed that the values calculated by Ally's correlation[4] are always lower than the experimental and calculated values obtained in the present study. The maximum relative deviation between our experimental values and those calculated with Ally's equation was around 7.4 %, while the relative root mean square (RMSD) was found to be 3.42%.

Conclusions

In this paper, we measured the vapor pressure of two alkaline nitrate/nitrite mixtures using a static method in the temperature range between 333.15 K and 473.15 K at 20 K intervals, and varying the total salt mass fraction between 0.50 and 0.95. Barker's method was successfully used to accurately calculate the liquid-phase composition at the equilibrium state from the total pressure and input sample composition and temperature. The experimental data concerning vapor pressure, and the temperature and liquid mass fraction were correlated using a polynomial equation. The calculated and measured data showed good agreement.

The vapor pressure of both mixtures showed similar behavior, but the risk of crystallization is lower for the working pair proposed by Vargas et al., which makes this more suitable for operating in absorption cycles driven by high temperature heat sources.

Acknowledgements. This study is part of an R&D project funded by the Spanish Ministry of Science and Innovation (ENE2007-65541/ALT). M. Álvarez acknowledges the Spanish Ministry of Science and Innovation for the award of a scholarship (BES-2008-006253).

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Table 1. Experimental vapor pressure data and calculated liquid mass fraction for both working pairs: $LiNO_3 + KNO_3 + NaNO_3$ in the mass ratio (53:28:19) and $LiNO_3 + KNO_3 + NaNO_2$ (53:35:12)

Davidson and Erickson[2] working pair				**Working pair of Vargas et al.[6]**			
$LiNO_3 + KNO_3 + NaNO_3$ (53:28:19)				$LiNO_3 + KNO_3 + NaNO_2$ (53:35:12)			
p/**kPa**	*w*	*p*/**kPa**	*w*	*p*/**kPa**	*w*	*p*/**kPa**	*w*
T=333.15 K		**T=353.15 K**		**T=333.15 K**		**T=353.15 K**	
12.38	0.4992	28.33	0.4994	12.72	0.4878	30.85	0.4880
10.40	0.5997	24.17	0.6000	9.45	0.6010	22.24	0.6011
6.31	0.6997	18.00	0.7000	6.92	0.7007	16.69	0.7009
		12.38	0.7493			12.35	0.7488
T=373.15 K		**T=393.15 K**		**T=373.15 K**		**T=393.15 K**	
60.13	0.4997	118.57	0.5004	64.52	0.4884	123.71	0.4890
48.49	0.6006	92.90	0.6015	48.41	0.6015	95.66	0.6021
36.46	0.7003	70.48	0.7008	34.96	0.7012	67.60	0.7017
26.54	0.7495	53.49	0.7500	28.16	0.7491	54.70	0.7495
20.32	0.8000	40.23	0.8004	21.47	0.7984	43.56	0.7988
13.61	0.8503	27.84	0.8506	14.13	0.8460	28.93	0.8463
T=413.15 K		**T=433.15 K**		**T=413.15 K**		**T=433.15 K**	
215.95	0.5014	377.13	0.5030	225.35	0.4900	364.04	0.4912
179.25	0.6033	292.92	0.6054	175.88	0.6032	302.62	0.6047
126.59	0.7017	220.38	0.7031	125.32	0.7027	216.32	0.7040
100.39	0.7508	175.32	0.7520	105.02	0.7504	180.69	0.7516
78.16	0.8011	140.91	0.8022	81.38	0.7996	142.07	0.8007
52.82	0.8511	93.25	0.8519	53.39	0.8468	89.89	0.8475
33.67	0.8998	59.32	0.9003	33.54	0.8989	58.33	0.8995
		38.36	0.9501			36.99	0.9494
T=453.15 K		**T=473.15 K**		**T=453.15 K**		**T=473.15 K**	
596.57	0.5050	920.02	0.5079	622.67	0.4935	965.22	0.4963
496.87	0.6092	789.60	0.6145	493.09	0.6070	764.93	0.6100
361.58	0.7051	564.39	0.7078	348.54	0.7059	552.82	0.7087
288.22	0.7537	451.19	0.7560	297.79	0.7534	463.65	0.7558
229.18	0.8036	357.82	0.8056	235.02	0.8023	368.22	0.8044
159.01	0.8531	249.55	0.8547	148.36	0.8485	238.02	0.8500
101.20	0.9011	162.51	0.9022	99.10	0.9003	164.46	0.9015
63.43	0.9506	99.24	0.9512	57.91	0.9499	87.96	0.9505

Table 2. Parameters of the analytical polynomial equation for $LiNO_3 + KNO_3 + NaNO_3$ in the mass ratio (53:28:19) and $LiNO_3 + KNO_3 + NaNO_2$ in the mass ratio (53:35:12)

	Davidson and Erickson's working pair[2] $LiNO_3 + KNO_3 + NaNO_3$ (53:28:19)	**Vargas et al.**[6] **working pair** $LiNO_3 + KNO_3 + NaNO_2$ (53:35:12)
a_0/**kPa**	8.7369	9.1810
a_1/**kPa**	27.0375	27.1205
a_2/**kPa**	-21.4172	-22.5826
b_0/**kPa.K**	-2432.1378	-2527.5165
b_1/**kPa.K**	-6955.3785	-7205.5897
b_2/**kPa.K**	4525.9568	5133.6024

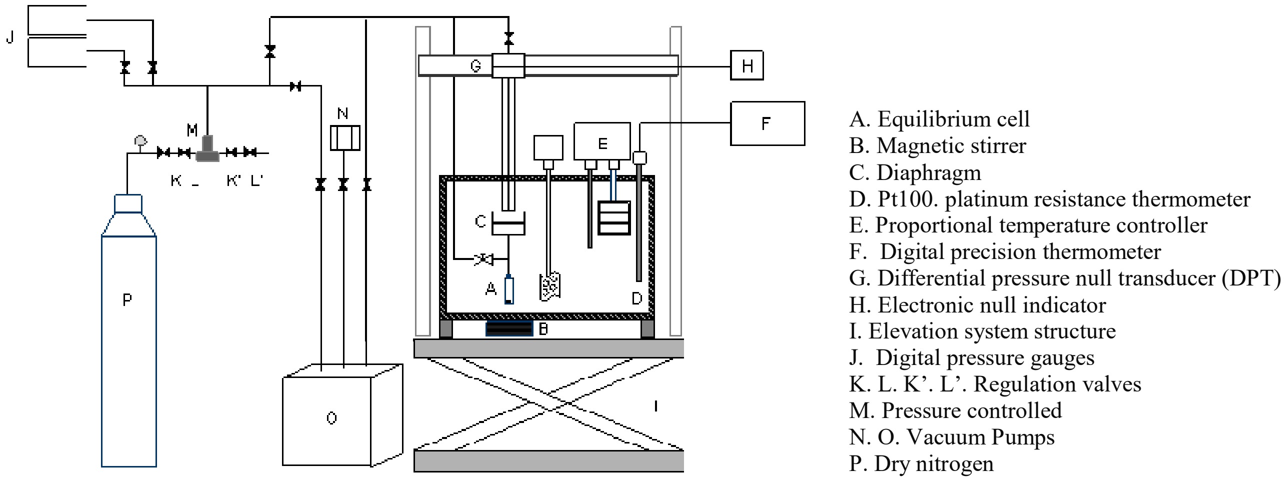


Figure 1. Experimental equipment used for liquid-vapor equilibrium measurements.

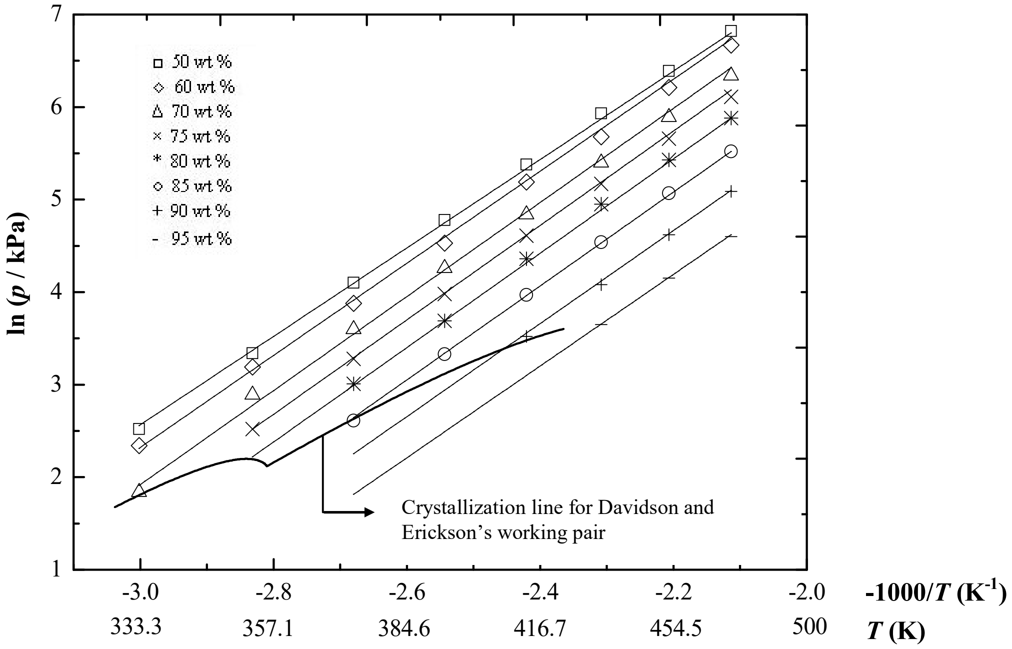
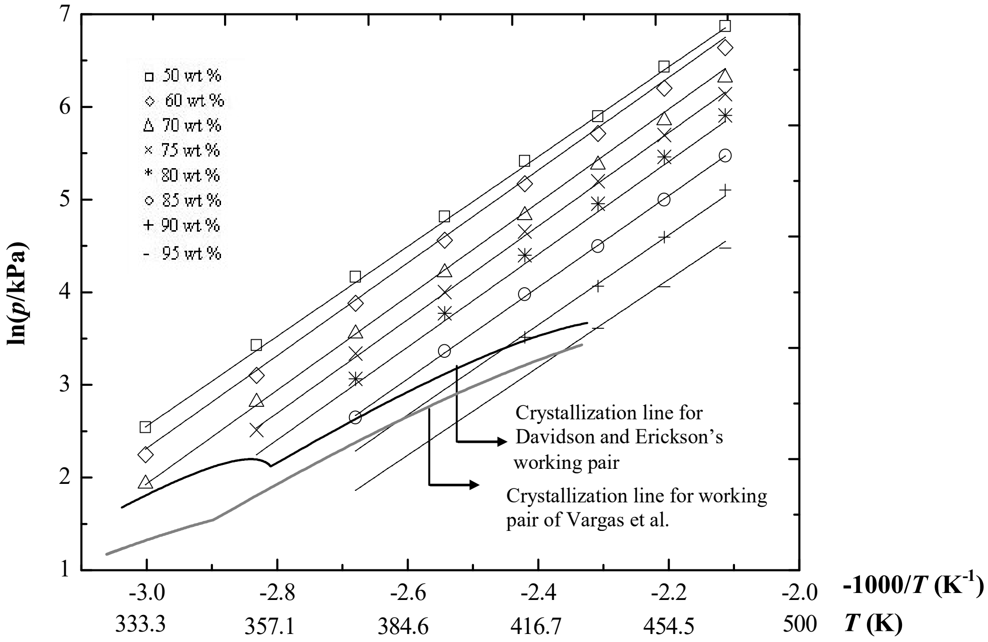


Figure 2. Dühring diagram for Davidson and Erickson's working pair[2] (Points: experimental data; Lines: pressure calculated using the analytical polynomial equation)



Crystallization line for Davidson and Erickson's working pair

Crystallization line for working pair of Vargas et al.

Figure 3. Dühring diagram for the working pair of Vargas et al.[6] (Points: experimental data; Lines: pressure calculated values using the analytical polynomial equation)

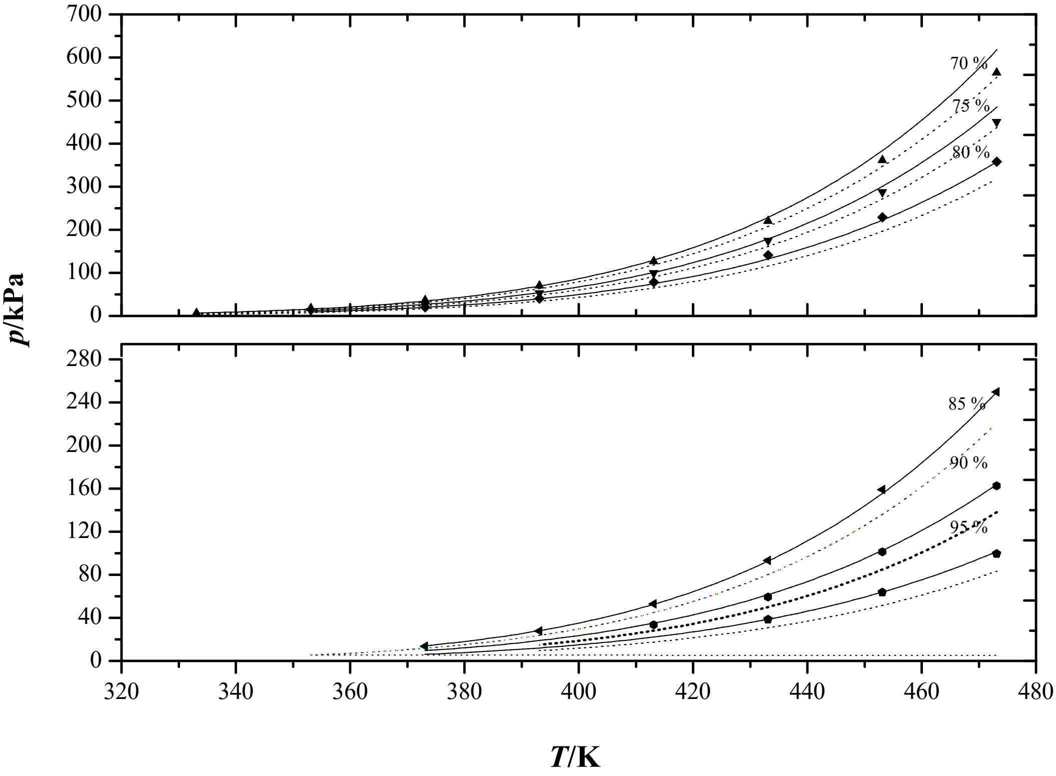


Figure 4. Vapor pressure for Davidson and Erickson's working pair (Points: experimental data; (—): pressure calculated values using the analytical polynomial equation; (- - -): calculated values using Ally's correlation)