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Notes

Solvent activity and osmotic pressure of binary aqueous and alcoholic solutions of calcium chloride up to 368 K and high salt concentration

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The solvent activity of aqueous and alcoholic liquid solutions of calcium chloride have been determined at ambient pressure, under vapor-liquid equilibrium conditions, and critically analyzed over a wide range of temperature (from ambient to ~368 K) and salt concentrations (from very dilute to nearly saturated solutions). The results are generally in good agreement with those reported or obtainable from a variety of literature data sources. In addition, for the alcoholic salted solutions, new T-concentrations regions have been explored. A solvation-dissociation based model was first parametrized and then used to establish the behavior of the activity of the solvents and to quantify the equilibrium vapor pressure lowering and the osmotic pressure of the solutions for any temperature and salt concentration. It was found that: a) activity of the solvents decreases when salt concentration increases, while it increases with temperature; b) osmotic pressure of concentrated solutions, is a function of both solvent activity and volumetric properties of the solutions, and is much higher (up to hundred-fold MPa for the aqueous solutions) of that calculated with the van't Hoff equation; c) the behavior of the osmotic pressure with the temperature is opposite to that predicted by the van't Hoff equation, coherently with the exothermic nature of the dilution process and the literature values of the heat of dilution.

Keywords: Solution chemistry, Solvent activity, Osmotic Pressure, Calcium Chloride

Adding a soluble salt to a solvent, results in a strong deviation from the ideal behavior of the mixture; the deviation usually increases with the solute concentration and is strongly dependent by the nature of the solvent[1]. When considering the binary liquid solutions of three major compounds as water, ethanol and calcium chloride, it comes out that: a) the binary unsalted mixture has been widely studied and its thermodynamic behavior is known very well; b) the salted aqueous solutions were also widely studied but the number of the available experimental data are from five to ten times less than that of the previous mentioned solutions, while the deviation from the ideal behavior is significantly higher; c) the number of available data for salted alcoholic solutions are much less, sometimes conflicting and restricted in narrow ranges of temperature and composition. On the other hand, aqueous and alcoholic solutions of calcium chloride are of great interest to explain natural phenomena involving the environment and the living organisms and for designing industrial and civil systems[1-4]. In previous works, we measured and simulated a number of thermodynamic properties of aqueous and alcoholic solutions of electrolytes[5-7] including the heat of dilution of aqueous and alcoholic solutions of calcium chloride[8-10], the density and the vapor pressure of the salted binaries[11] and of the ternary system made of water, ethanol and calcium chloride[12]. Some of these data were also used to simulate the extractive distillation of ethanol from dilute aqueous solution[13]. The purpose of the present work is to reconsider the density and the vapor pressure data of salted binary solutions in terms of solvent activity, vapor pressure lowering and molar volume, to predict the behavior of these properties over a wide range of temperature (from ambient to about 368 K) and salt concentration (from very dilute to almost saturated salt solutions), including T-concentration regions not explored before, thus resolving some contradictions existing in the literature. In this context, smoothed literature values of the vapor pressure of each pure solvent, P^0, were used[14, 15]. The activity of the solvents and the volumetric properties of the solutions were then used for calculating the osmotic pressure. In fact, while this property is often considered as another way of expressing the activity of the solvent of a solution[16], it is reasonable to expect that the molar volume of the solution could deviate significantly from linearity for high mole fraction of the salt and, consequently, the osmotic pressure of the solution would be affected by both the activity and the partial molar volume of the solvent. An additional question to be clarified is concerned with the expected dependence of the osmotic pressure with the temperature considering that, in the case like the one under examination, one would expects a behavior opposite to that given by the van't Hoff equation.

Theory

According to Blandamer *et al.*[1] and to Bechtold and Newton[17], under pressure and temperature conditions of interest of this study, the experimental activity of the solvents is given by the ratio of the pressure of the vapor in equilibrium with the liquid, and the vapor pressure of the pure solvent at the same temperature of the solution. In fact, it can be safely assumed that the vapor phase behaves ideally[18, 19], thus avoiding needless complication in the analysis of the experimental data. To simulate the behavior of the two systems under considerations, the values of the solvent activity, a_s, were calculated with a semi-empirical solvation-dissociation model in combination with the NRTL equation[20] for the activity coefficient of the free solvent, in aqueous and alcoholic salt solutions.

$$a_s = \gamma_s x_s \qquad \text{... (1)}$$

where x_s is the mole fraction of the free solvent in the salt solutions and γ_s is the corresponding activity coefficient.

For aqueous salt solutions, x_s, was calculated by Eq. 2, where x_s^* and $(1-x_s^*)$ represent the stoichiometric mole fraction of the solvent and of the salt, respectively. Assuming that the salt is completely dissociated and h is equal to $h_\infty(1-x_s^*)^4$, after an inspection of the results obtained by Ohe [21], the final equation for the mole fraction of free water, x_s, is

$$x_s = \frac{x_s^* - 3h_\infty(1-x_s^*)^5}{x_s^* - 3(1-x_s^*)[h_\infty(1-x_s^*)^4 - 1]} \qquad \text{...(2)}$$

The number of moles of free water, n_W, are related to the mean solvation number and to the number of the stoichiometric moles of water, n_W^*, and salt, n_{salt}^*, by the following equation.

$$n_W = n_W^* - 3hn_{salt}^* \qquad \text{... (3)}$$

The total number of moles in the mixtures is obtained by adding 3×n_{salt}^* to n_W. Consequently,

$$x_s = n_W^* - 3n_{salt}^*(h-1) \qquad \text{... (4)}$$

Equation 4 is equal to Eq. 2, since x_s^* is the ratio between n_W^* and $(n_W^* + n_{salt}^*)$.

The true mole fractions of ethanol in the salt alcoholic solutions, x_s, were calculated by Eq. 5, assuming that the mean solvation number is practically nil and the number of the moles of ions plus those of undissociated salt were proportional to $(1-x_s^*)$ through an adjustable model parameter ν.

$$x_s = \frac{x_s^*}{x_s^* + \nu(1-x_s^*)} \qquad \text{...(5)}$$

The activity coefficients of the solvent~~s~~ in the salted pseudo-binary solutions, γ_s, were calculated using the NRTL equation

$$\ln(\gamma_s) = (1-x_s)^2 \left[\tau_{21}\left(\frac{G_{21}}{x_s + (1-x_s)G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{\left((1-x_s) + x_s G_{12}\right)^2} \right] \qquad \text{...(6)}$$

with

$G_{12} = \exp(-0.3031\tau_{12})\,;\, G_{21} = \exp(-0.3031\tau_{21})\,;$
and $\tau_{12} = \dfrac{\delta_{12}}{T};\, \tau_{21} = \dfrac{\delta_{21}}{T}$

The values of the three adjustable parameters of the model (δ_{12}, δ_{21} and h_∞ for the aqueous solutions; δ_{12}, δ_{21} and ν for the alcoholic solutions), were found by minimizing the following functions

$$\Phi_W(h_\infty, \delta_{12}^W, \delta_{21}^W) = \sum_{i=1}^{N}\left(a_W^{cal} - a_W^{exp}\right)^2 \qquad \text{...(7)}$$

$$\Phi_E(\nu, \delta_{12}^E, \delta_{21}^E) = \sum_{i=1}^{N}\left(a_E^{cal} - a_E^{exp}\right)^2 \qquad \text{...(8)}$$

where a_W^{exp} and a_W^{cal} are the measured and calculated activity of the free water, respectively, and a_E^{exp} and a_E^{cal} are the measured and calculated activity of the free ethanol, respectively, in the pseudo-binary salt solutions. Equations 9 and 10 were then used to calculate the vapor pressure lowering, ΔP, and the osmotic pressure, Π, respectively, of the salted mixtures, as function of both temperature and salt concentration

$$\Delta P = (P_s^0 - P) = P_s^0(1-a_s) \qquad \text{...(9)}$$

$$\Pi = \frac{-\ln(a_s)RT}{\overline{V_s}} \qquad \text{...(10)}$$

According to Li and Lee[21], the partial molar volume of the solvent in the solution, $\overline{V_s}$, could be approximated with the molar volume of the pure solvent, V_s^0. However, it is necessary to verify the limits of applicability of this approximation. To this purpose and according to Abdulagatov *et al.*[22] and Zezin *et al.*[23], density data of salted aqueous and alcoholic solutions, ρ, along with the corresponding molality, m, and smoothed density data for water[24] and ethanol[25, 26] at the same temperature (ρ_s^0), were used for quantifying the value of the apparent molar volume, V_ϕ, of the salt using Eq. 11

$$V_\phi = \frac{1000(\rho_s^0 - \rho)}{m\rho_s^0\rho} + \frac{110.98}{\rho} \qquad \text{...(11)}$$

Then, this quantity was used to calculate the molar volume, V_m, of the solutions as function of the temperature and of the stoichiometric mole fraction of the solvent using Eq. 12.

$$V_m = \frac{x_s^* M}{\rho_s^0} + (1 - x_s^*) V_\phi \qquad ...(12)$$

where M = 18.02 for water and M = 46.07 for ethanol

The density of the solutions was calculated using Eq. 13 for aqueous solutions and Eq. 14 for alcoholic solutions, which were obtained by assuming that, for fixed T and stoichiometric weight fraction of the solvent, ω_s, it is additive with respect to the densities of the solvent, ρ_S^0, and of the dissolved salt, ρ_{DS}; furthermore, it was assumed that ρ_{DS} depends linearly by the concentration for any fixed value of T.

$$\rho = \rho_W^0 \omega_W + \begin{Bmatrix} -10^{-3} \begin{bmatrix} 0.7644(1-\omega_W) \\ +0.5135 \end{bmatrix} T \\ +0.46321(1-\omega_W) \\ +1.8\ 1431 \end{Bmatrix} \qquad ...(13)$$

$$\omega_W = \frac{x_W^*}{6.1587 - 5.1587 x_W^*} \ ; \ T\ °C$$

$$\rho = \rho_E^0 \omega_E + \begin{Bmatrix} \begin{bmatrix} 0.00305(1-\omega_E) \\ -0.001621 \end{bmatrix} T \\ +0.17138(1-\omega_E) \\ +1.57176 \end{Bmatrix} (1-\omega_E) \qquad ...(14)$$

$$\omega_E = \frac{x_E^*}{2.4089 - 1.4089 x_E^*} \ ; \ T\ °C$$

Smoothed literature data[24] covering the whole ranges of temperature and concentration of interest for this work, were used to parameterize Eq. 13. The accuracy of equation is satisfactory as shown by the values of the average relative deviation (ARD = 0.06%), of the maximum relative deviation (MRD = 0.2%), and of the multiple correlation coefficient (R^2 = 0.99). The density of alcoholic solutions of calcium chloride are not available over the entire range of temperature and concentration considered in this study; to our best knowledge the most complete set of data is that reported by Hayward and Perman[27] which ranges from 295 K to 333 K and from 2.71 to 28.3 (wt%) of salt. The accuracy of these data was verified using Eq. 14, parameterized with the experimental data previously cited[11]. It has been verified, by evaluating the extrapolation performance of Eq. 13, that Eq. 14 can be used safely for extrapolating the density of alcoholic salted solutions to higher temperature and concentrations close to the saturation with estimated values of ARD and MRD of about 0.2% and 0.9%, respectively.

Results and discussion

The experimental and calculated values of the solvent activity and vapor pressure lowering for aqueous and alcoholic solutions of calcium chloride are reported in Table 1 and Table S1 (Supplementary data), along with the corresponding differences. The experimental and calculated molar volume of the alcoholic solution of calcium chloride are reported in Table S2 (Supplementary data), along with the corresponding differences.

The values of the model parameters are reported in Table S3 (Supplementary data), along with the corresponding standard errors, the standard error (SE) for the activity of the solvents, the AAD for the pressure lowering, and the values of the square root of the multiple correlation coefficients, R. Specifically, SE(a_S) is obtained as the ratio of the square root of Φ_S and the number of experimental data while, AAD is the ratio of the sum of the absolute average difference between ΔP^{cal} and ΔP^{exp}, and the number of experimental data.

Figures 1 and 2 show the calculated behavior of the activity of water and ethanol as function of temperature and salt concentration, for comparison with the data reported in Table 1 and Table S1, and several sets of literature data. As can be seen the agreement is satisfactory considering the width of the ranges of temperature and salt concentration; from ambient up to about 368 K, and from very dilute to almost saturated solutions. It is worthwhile to emphasize that, in both systems, the activity of the solvent increases with the temperature; this behavior is in agreement with that of several literature sets of data, with some minor exception, and with that reported by Conde-Petit[3] for aqueous solutions of calcium chloride. Similarly, Figs 3 and 4 show the good agreement between experimental and calculated equilibrium pressure lowering for both the systems under examination with the data reported in Table 1 and Table S1, and with several sets of literature data. In addition, Figs 2 and 4 show the capability of the model in predicting the ethanol activity and vapor pressure lowering outside the range of temperature experimentally investigated in the present study. Figs 5 and 6 show the behavior of the molar volume of the salted solutions calculated with Eqs 11 and 12 as function of the temperature and of the mole fraction of the salt; as can be seen, when the concentration of the solute is higher than 35-40% the lines deviates significantly from linearity and, consequently, the partial molar volume of the solvent is significantly lower than the molar volume of the pure solvent. Actually, as can be seen from

Table 1—Experimental and calculated values of solvent activity and vapor pressure lowering for aqueous and alcoholic solutions of $CaCl_2$ with respect to pure solvents at temperature T, percent by weight of salt and ambient pressure[a]

Salt conc. (wt%)	T (K)	a_s^{cal}	a_s^{exp}	Δa_s	ΔP^{cal} (kPa)	ΔP^{exp} (kPa)	$\Delta(\Delta P)$ (kPa)
			Water + $CaCl_2$				
5.84	303.15	0.967	0.933	0.034	0.14	0.28	- 0.14
12.65	303.15	0.910	0.940	- 0.030	0.38	0.26	0.12
17.73	303.15	0.847	0.893	- 0.046	0.65	0.46	0.19
27.47	303.15	0.669	0.644	0.025	1.40	1.51	- 0.11
31.30	303.15	0.585	0.572	0.013	1.76	1.82	- 0.06
5.84	313.15	0.968	0.991	- 0.023	0.24	0.07	0.17
12.65	313.15	0.913	0.937	- 0.024	0.64	0.47	0.17
17.73	313.15	0.853	0.864	- 0.011	1.08	1.00	0.08
27.47	313.15	0.684	0.671	0.013	2.33	2.43	- 0.10
31.30	313.15	0.603	0.629	- 0.026	2.93	2.73	0.20
3.55	323.15	0.982	0.985	- 0.003	0.23	0.18	0.05
5.84	323.15	0.968	0.968	0.000	0.39	0.40	- 0.01
8.45	323.15	0.951	0.936	0.015	0.61	0.78	- 0.17
12.65	323.15	0.915	0.917	- 0.002	1.04	1.02	0.02
12.88	323.15	0.913	0.888	0.025	1.07	1.38	- 0.21
17.73	323.15	0.858	0.865	- 0.007	1.75	1.66	0.11
18.11	323.15	0.853	0.829	0.024	1.81	2.10	- 0.29
22.59	323.15	0.786	0.762	0.014	2.63	2.93	- 0.20
26.86	323.15	0.710	0.711	- 0.001	3.58	3.56	0.02
27.47	323.15	0.698	0.700	- 0.002	3.73	3.70	0.03
28.89	323.15	0.669	0.673	- 0.004	4.08	4.04	0.04
31.00	323.15	0.625	0.599	0.026	4.62	4.94	- 0.32
35.90	323.15	0.519	0.511	0.008	5.93	6.02	- 0.07
39.70	323.15	0.438	0.464	- 0.026	6.93	6.61	0.32
40.43	323.15	0.422	0.447	- 0.025	7.12	6.82	0.30
48.34	323.15	0.274	0.271	0.003	8.95	8.98	- 0.03
3.55	333.15	0.982	0.983	- 0.001	0.36	0.33	0.03
5.84	333.15	0.969	0.978	- 0.009	0.63	0.43	0.20
12.65	333.15	0.917	0.936	- 0.019	1.65	1.28	0.37
12.88	333.15	0.915	0.927	- 0.012	1.69	1.45	0.24
17.73	333.15	0.863	0.871	- 0.008	2.73	2.56	0.17
18.11	333.15	0.858	0.856	0.002	2.83	2.87	- 0.04
22.59	333.15	0.794	0.788	- 0.006	4.10	4.21	- 0.11
26.86	333.15	0.721	0.724	- 0.003	5.56	5.49	0.07
27.47	333.15	0.709	0.709	0.000	5.79	5.79	0.00
28.89	333.15	0.682	0.685	- 0.003	6.33	6.28	0.05
31.00	333.15	0.640	0.644	- 0.004	7.18	7.08	0.10
35.90	333.15	0.536	0.533	0.003	9.24	9.31	- 0.07
39.70	333.15	0.455	0.465	- 0.010	10.85	10.65	0.20
40.43	333.15	0.440	0.457	- 0.017	11.16	10.81	0.35
48.34	333.15	0.290	0.290	0.000	14.15	14.15	0.00
			Ethanol + $CaCl_2$				
2.72	303.15	0.988	0.974	0.014	0.12	0.27	- 0.15
4.90	303.15	0.978	0.966	0.012	0.23	0.36	- 0.13
7.92	303.15	0.960	0.947	0.013	0.42	0.56	- 0.14
8.78	303.15	0.954	0.947	0.007	0.49	0.56	- 0.07
12.07	303.15	0.924	0.902	0.022	0.81	1.03	- 0.22
15.28	303.15	0.886	0.897	- 0.011	1.20	1.08	0.12
16.78	303.15	0.865	0.868	- 0.004	1.42	1.39	0.03

(*Contd.*)

Table 1—Experimental and calculated values of solvent activity and vapor pressure lowering for aqueous and alcoholic solutions of $CaCl_2$ with respect to pure solvents at temperature T, percent by weight of salt and ambient pressure[a] (*Contd*.)

Salt conc. (wt%)	T (K)	$\boldsymbol{a_s^{cal}}$	$\boldsymbol{a_s^{exp}}$	$\Delta\boldsymbol{a_s}$	$\Delta\boldsymbol{P^{cal}}$ (kPa)	$\Delta\boldsymbol{P^{exp}}$ (kPa)	$\Delta(\Delta\boldsymbol{P})$ (kPa)
20.76	303.15	0.804	0.804	0.000	2.07	2.07	0.00
2.72	313.15	0.988	0.992	- 0.003	0.21	0.15	0.06
4.90	313.15	0.978	0.981	- 0.003	0.38	0.33	0.05
7.92	313.15	0.961	0.959	0.002	0.69	0.73	- 0.04
8.78	313.15	0.956	0.948	0.008	0.79	0.93	- 0.14
12.07	313.15	0.928	0.921	0.007	1.28	1.41	- 0.13
15.28	313.15	0.894	0.903	- 0.009	1.89	1.73	0.16
16.78	313.15	0.875	0.875	0.000	2.23	2.24	- 0.01
20.76	313.15	0.819	0.831	- 0.012	3.24	3.01	0.23
2.72	333.15	0.988	0.986	0.002	0.34	0.42	- 0.08
4.90	323.15	0.979	0.981	- 0.002	0.63	0.55	0.08
7.92	323.15	0.963	0.964	- 0.001	1.10	1.07	0.03
8.78	323.15	0.957	0.955	0.002	1.26	1.34	- 0.08
12.07	323.15	0.932	0.929	0.003	1.10	2.10	- 1.00
15.28	323.15	0.901	0.900	0.001	2.92	2.94	- 0.02
16.78	323.15	0.884	0.884	0.000	3.42	3.42	0.00
20.76	323.15	0.832	0.836	- 0.004	4.96	4.83	0.13
2.72	333.15	0.988	0.990	- 0.002	0.55	0.49	0.06
4.90	333.15	0.979	0.979	0.000	0.99	0.98	0.01
7.92	333.15	0.964	0.965	- 0.001	1.71	1.62	0.09
8.78	333.15	0.959	0.954	0.005	1.95	2.17	- 0.22
12.07	333.15	0.935	0.935	0.000	3.03	3.03	0.00
15.28	333.15	0.906	0.907	- 0.001	4.39	4.38	0.01
16.78	333.15	0.891	0.896	- 0.005	5.12	4.86	0.26
20.76	333.15	0.843	0.845	- 0.002	7.38	7.29	0.09
38.65	333.15	0.551	0.560	- 0.009	21.05	20.67	0.38

[a] wt% is the percent by weight of dissolved $CaCl_2$; a_s^{cal} and a_s^{exp} are the calculated and experimental activity of the solvent, respectively; Δa_s is the difference between a_s^{cal} and a_s^{exp}; ΔP^{cal} and ΔP^{exp} are the calculated and experimental pressure lowering, respectively; $\Delta(\Delta P)$ is the difference between ΔP^{cal} and ΔP^{exp}.

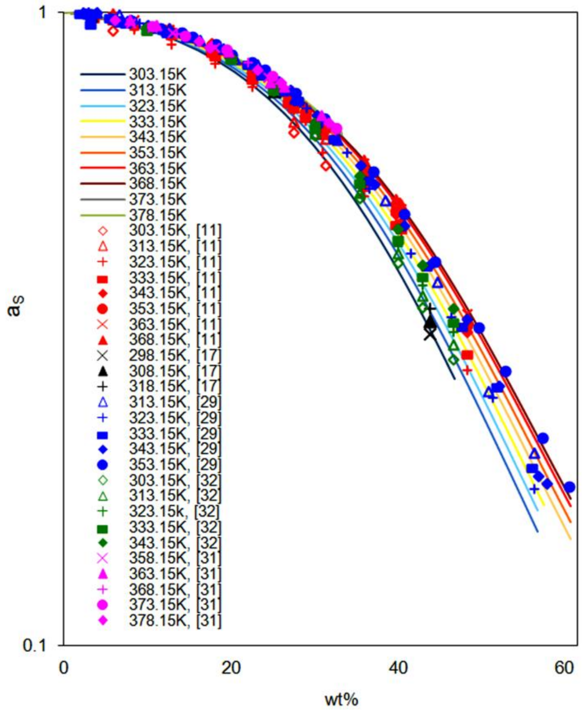

Fig. 1—Experimental and calculated activity of water as function of temperature and $CaCl_2$ concentration.

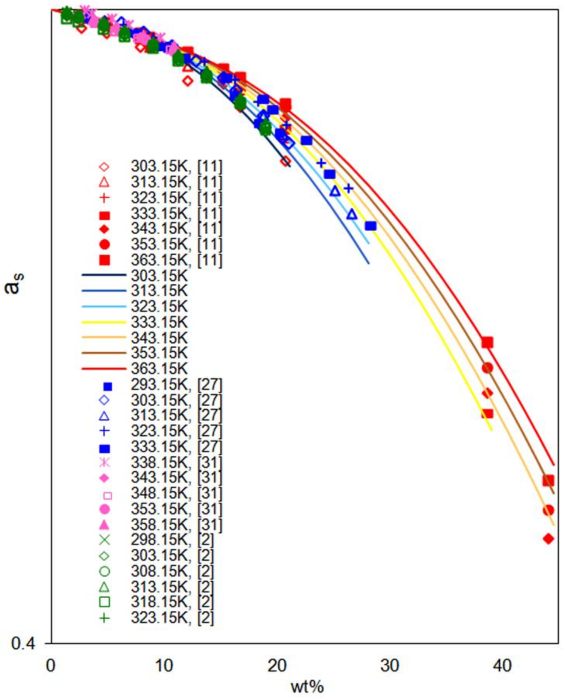

Fig. 2—Experimental and calculated activity of Ethanol as function of temperature and $CaCl_2$ concentration

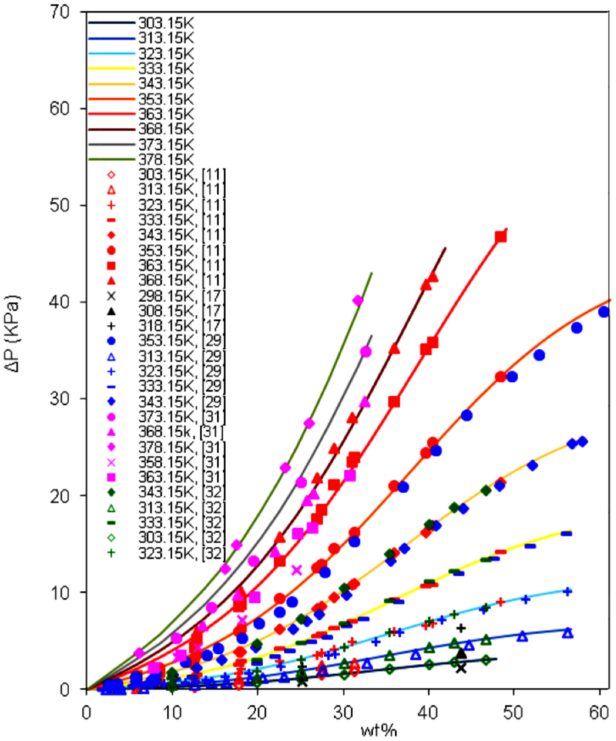

Fig. 3—Experimental and calculated vapor pressure lowering as function of temperature and $CaCl_2$ concentration, for aqueous solutions

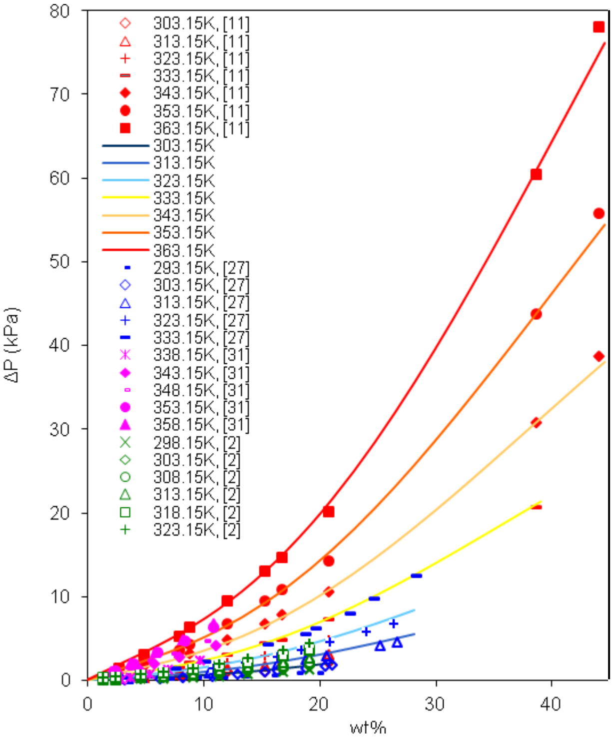

Fig. 4—Experimental and calculated vapor pressure lowering as function of temperature and $CaCl_2$ concentration, for alcoholic solutions

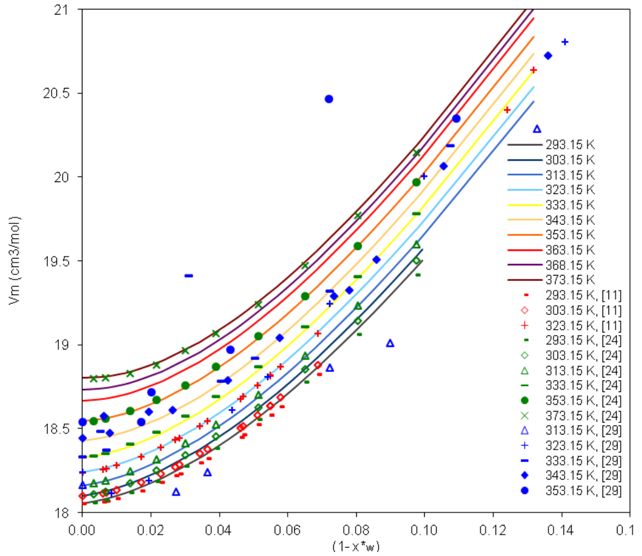

Fig. 5—Experimental and calculated molar volume of aqueous solutions of $CaCl_2$

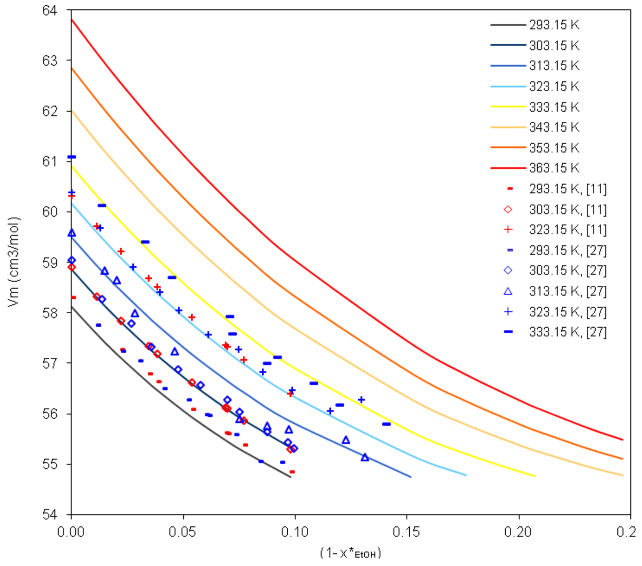

Fig. 6—Experimental and calculated molar volume of alcoholic solutions of $CaCl_2$

Figs 5 and 6, this phenomenon is much more important for the aqueous solutions where the prevailing interactions are between water and ions. May be worth to emphasize that this is in accordance with the well known salting out effect exerted by calcium chloride on the water-ethanol mixtures.

Further, Figs 7 and 8 show the behavior of the osmotic pressure of aqueous and alcoholic solutions of $CaCl_2$ calculated with the non-simplified vant' Hoff equation[16, 21, 27, 28], Eq. 10, for comparison with the corresponding behavior calculated from the van't

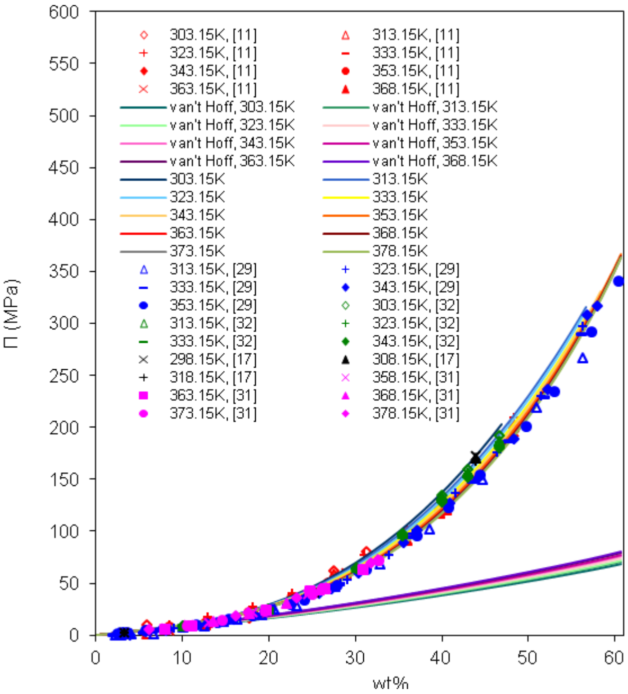

Fig. 7—Deviation from the ideal behavior of the osmotic pressure as function of temperature and $CaCl_2$ concentration, for aqueous solutions

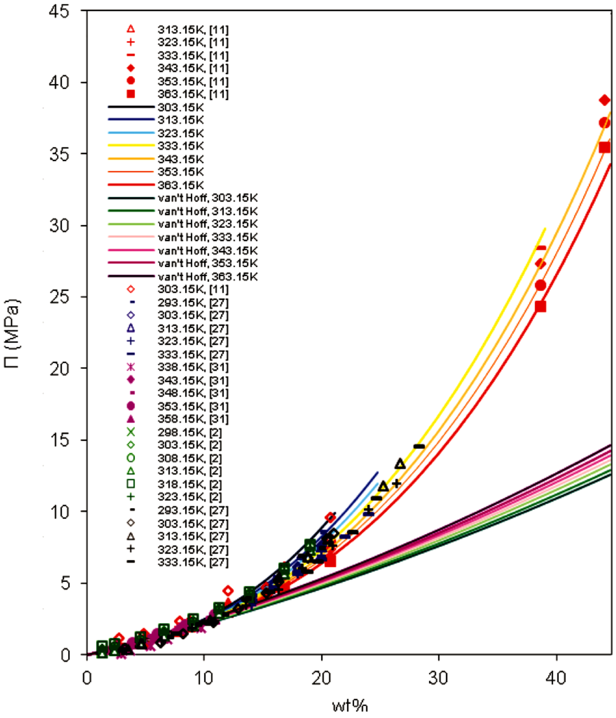

Fig. 8—Deviation from the ideal behavior of the osmotic pressure as function of temperature and $CaCl_2$ concentration, for alcoholic solutions

Hoff equation, which can only be applied to very dilute salt solutions. As can be seen from Figs 1–6, deviation from ideal behavior increases significantly with the concentration of the salt for both aqueous and alcoholic solutions while the influence of the temperature is opposite. Furthermore, the values of the osmotic pressure calculated with Eq. 10, agree reasonably well with the values calculated using the solvent activity data reported in Table 1 and Table S1 and with the solvent activity obtained from several sets of literature data, using the partial molar volume calculated by Eqs 11-14 along with standard thermodynamics. Finally, it is worthwhile to note that the real dependence of the osmotic pressure by the temperature, resulting from this work, is consistent with the fact that the osmosis is a dilution process and, in the present case, this process is exothermic[8-10, 27, 29, 30].

Conclusions

The results of this study show clearly that, under ambient pressure, the activity and the partial molar volume of the solvent in aqueous and in alcoholic solutions of calcium chloride are the chief properties, which have to be taken into account for predicting several quantities of practical and industrial interest. Specifically, it was found that from ambient to nearly 368 K and from very dilute solutions to nearly 50% by weight of salt, (a) the activity of the solvent decreases significantly with the salt concentration and increases with the temperature, and, (b) the molar volume of the mixtures deviates significantly from the linear behavior, and, for high salt concentration, the partial molar volume of the solvent is significantly different from the molar volume of the pure solvent. It is worthwhile to note that the osmotic pressure calculated in this way is of one order of magnitude higher than that predicted by the van't Hoff equation and can reach very high values, around 400 MPa for aqueous solutions and 50 MPa for alcoholic solutions. Finally, it has been found that the osmotic pressure decreases with the temperature, in accordance with the exothermic nature of the dilution process and the literature values of the heat of dilution.

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