Vapor Pressure Measurements of Binary Solutions of $CaCl_2$ with Methanol and Ethanol at T = (298.15 to 323.15) K Using a Static Method

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Vapor pressures p of $CaCl_2 + CH_3OH$ and $CaCl_2 + C_2H_5OH$ at T = (298.15 to 323.15) K were measured, osmotic (ϕ) and activity (γ) coefficients and activity of solvent (a_s) have been evaluated. The experiments were carried out for $CaCl_2 + CH_3OH$ solutions in a molality range m = (0.10402 to 2.59613) mol·kg^{-1} and for $CaCl_2 + C_2H_5OH$ solutions in a molality range m = (0.12359 to 2.12091) mol·kg^{-1}. The Antoine equation for the empirical description of the experimental vapor pressure results and the Pitzer−Mayorga model with inclusion of ionic strength dependence of the third virial coefficient for the description of calculated osmotic coefficients were used. The parameters of Pitzer−Mayorga model were used for evaluation of activity coefficients.

Introduction

The search of new refrigerant and heat transfer fluids for absorption refrigeration machines and absorption heat pumps and the development of efficient processes of their use become scientifically and practically important and have received growing attention in recent years from the refrigeration and air-conditioning industry, especially the aspects of energy-saving and protection of the environment. The efficiency of an absorption refrigeration machine and heat pump cycles are largely dependent on the physical and chemical properties of the heat transfer fluids. The application of $CaCl_2$ solutions of alcohols in absorption systems were discussed in refs 1 and 2.

The present study is an effort to extend the information of the vapor pressure of $CaCl_2 + CH_3OH$ and $CaCl_2 + C_2H_5OH$ solutions as potential refrigerants and heat transfer fluids. Previous investigations[3−8] on the vapor pressure of these solutions are tabulated in Table 1. The experiments were carried out in the temperature range T = (298.15 to 323.15) K and at molalities of $CaCl_2$ m = (0.10402 to 2.59613) mol·kg^{-1} in methanol and m = (0.12359 to 2.12091) mol·kg^{-1} in ethanol. From the data the osmotic and activity coefficients (γ and ϕ) and activity of solvent (a_s) have been evaluated.

Experimental Section

The experiments to determine the vapor pressure of $CaCl_2 + CH_3OH$ and $CaCl_2 + C_2H_5OH$ solutions were performed in a glass cell by using a static method.[9] The experimental set up consisted of a bolted-top cell with an internal volume of 95.64 cm^3 surrounded by a water bath, which was kept at constant temperature (± 0.02 K) using a thermostat. The temperature inside the cell was measured by a platinum resistance thermometer PT-100 (type 42441-V100), connected to the signal conditioner Kelvimat type 4303, with an accuracy of ± 0.01 K. The pressure was measured using a calibrated high accuracy sensor head (type 615A, MKS Baratron) connected to the signal conditioner (type 670A, MKS Baratron) attached to the top of the cell. The sensor head and the connecting line from the cell to the sensor were thermostated at 333.15 ± 0.01 K. This temperature is always kept above the temperatures of the measuring cell in order to avoid any condensation in the pressure head. The cell is kept at room temperature under vacuum for ca. 12 h (until the pressure sensor indicate zero point). Exactly known amounts of the solution were injected stepwise into the thermostated equilibrium cell with the help of special glass injectors. Phase equilibrium was reached in each step by using a magnetic stirrer with a Teflon-coated magnet inside the cell. Equilibration in the cell is a rapid process, and a constant pressure was reached within 15 min. Equilibrium pressure readings were registered in 10 min intervals. The concentrations of solutions were changed by adding certain amount of pure solvent to a starting solution placed in the cell. Prior to injection into the measuring cell, the pure solvent is degassed in the special designed cell using the rotary vane vacuum pump. The injection cell is weighed before and after injection. The experimental uncertainties were $\Delta T = \pm$ 0.01 K for temperature and $\Delta p = \pm$ 10 Pa for pressure. The measured vapor pressures are reliable to within an average uncertainty ± 0.05 % according to test measurements.[9−10]

Methanol (w > 0.998), ethanol (w > 0.998), and $CaCl_2$ (w > 0.998) were purchased from Merck, Germany. $CaCl_2$ was used without further purification; however, the salt was dried in a special cell at 413.15 K and under vacuum using a TRIVAC rotary vane vacuum pump for 24 h prior to use. The cell was kept at room temperature under vacuum for 12 h. The solutions were prepared by mass using a BP 221 S electronic scale (Sartorius AG) with a resolution of 0.0001 g.

Results and Discussion

In this work, the vapor pressure of $CaCl_2 + CH_3OH$ solutions in the molality range m = (0.10402 to 2.59613) mol·kg^{-1} and of $CaCl_2 + C_2H_5OH$ solutions in the molality range m = (0.12359 to 2.12091) mol·kg^{-1} at T = (298.15 to 323.15) K were measured. From the data the osmotic and activity coefficients (γ and ϕ) and activity of solvent (a_s) have been evaluated. The measured vapor pressures are listed in Table 2. The plot of the vapor pressure results of $CaCl_2 + CH_3OH$ and of $CaCl_2 + C_2H_5OH$ solutions against molality (m) of $CaCl_2$ together with literature values at T = 298.15 K are shown in Figures 1 and 2.

The experimental vapor pressure results were compared with the available literature results at 298.15 K. The average deviation

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Table 1. Literature Review of Vapor Pressure Measurements of Investigated Solutions

first author	reference	year	method[a]	properties	uncertainty	temperature/K	concentration, m/(mol·kg^{-1})
$CaCl_2 + CH_3OH$							
Bixon	3	1979	OS	p	±0.1 mmHg	298.05	0.3186 to 2.6345
Uchizono	4	1983	FM	a	±0.5 mmHg	298.15	0.200 to 2.726
Hongo	5	1990	FM	p, a	<2 %	298.15	0.200 to 2.603
Yamamoto	6	1995	SM	p, a	±0.01 %	298.15	0.328 to 2.258
Zafarani-Moattar	7	2002	IP	ϕ, p	±0.0002	298.15	0 to 3.7250
$CaCl_2 + C_2H_5OH$							
Uchizono	4	1983	FM	a	±0.5 mmHg	298.15	0.200 to 2.201
Hongo	5	1990	FM	p, a	<2 %	298.15	0.301 to 2.205
Yamamoto	6	1995	SM	p, a	±0.01 %	298.15	0.311 to 1.879
Zafarani-Moattar	8	2000	IP	p, ϕ, a	±0.0002	298.15	0.1362 to 2.3717

[a] OS, Othmer still; FM, flow method; SM, static method; IP, isopiestic method; p, vapor pressure; a, activity of solvent; ϕ, osmotic coefficient; m, molality.

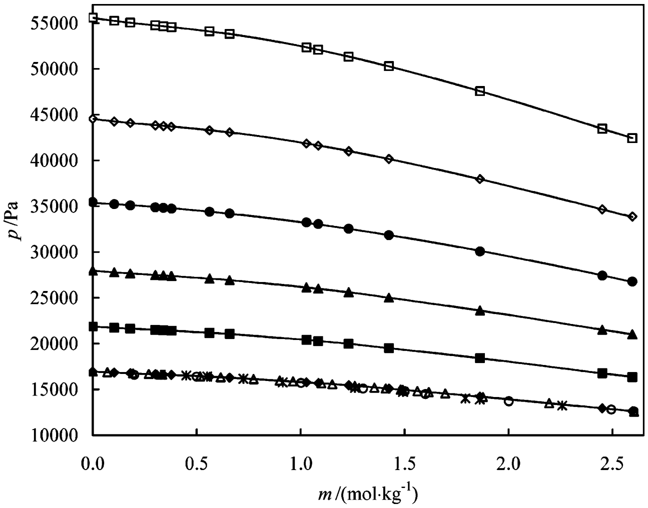

Figure 1. Vapor pressure p of $CaCl_2 + CH_3OH$ solutions vs molality m of $CaCl_2$: ◆, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ●, 313.15 K; ◇, 318.15 K; □, 323.15 K; ○, Hongo et al.[5] at $T = 298.15$ K; *, Yamamoto et al.[6] at $T = 298.15$ K; △, Zafarani-Moattar et al.[7] at $T = 298.15$ K; —, Antoine equation.

Table 2. Experimental Vapor Pressure Values of the Investigated Solutions

	p/Pa					
m/ (mol·kg^{-1})	$T =$ 298.15 K	$T =$ 303.15 K	$T =$ 308.15 K	$T =$ 313.15 K	$T =$ 318.15 K	$T =$ 323.15 K
$CaCl_2 + CH_3OH$						
0.10402	16849	21742	27785	35232	44270	55265
0.18097	16774	21649	27670	35093	44100	55059
0.30129	16663	21509	27501	34888	43850	54764
0.34007	16625	21465	27444	34818	43771	54665
0.37895	16589	21418	27388	34752	43695	54576
0.56187	16400	21185	27104	34417	43301	54126
0.65834	16293	21053	26944	34223	43069	53843
1.02825	15778	20406	26144	33236	41865	52354
1.08516	15689	20289	25997	33061	41637	52102
1.23112	15448	19990	25608	32555	41022	51355
1.42494	15093	19523	25018	31863	40162	50307
1.86317	14212	18411	23617	30068	37970	47575
2.45128	12939	16770	21527	27435	34672	43479
2.59613	12635	16360	21011	26778	33887	42429
$CaCl_2 + C_2H_5OH$						
0.12359	7820	10391	13666	17777	22902	29257
0.21856	7785	10345	13607	17701	22806	29137
0.43590	7691	10223	13450	17501	22555	28823
0.63208	7600	10103	13296	17306	22306	28516
0.89583	7464	9928	13070	17013	21942	28060
1.14832	7321	9743	12830	16706	21549	27566
1.44645	7132	9496	12509	16296	21031	26909
1.81882	6856	9131	12036	15693	20263	25943
2.12091	6602	8793	11599	15133	19552	25057

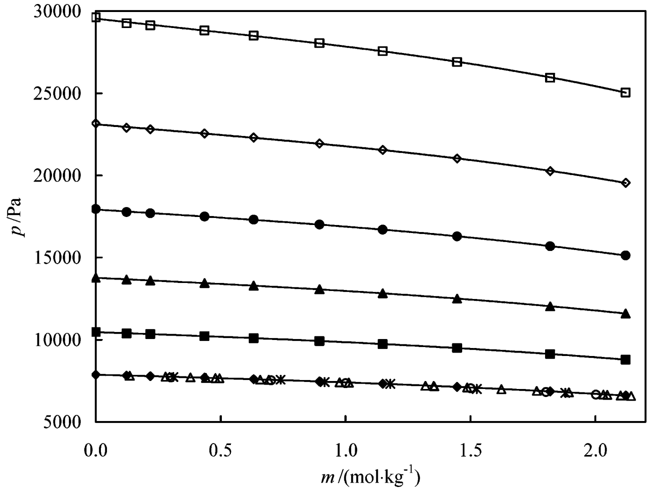

Figure 2. Vapor pressure p of $CaCl_2 + C_2H_5OH$ solutions vs molality m of $CaCl_2$: ◆, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ●, 313.15 K; ◇, 318.15 K; □, 323.15 K; ○, Hongo et al.[5] at $T = 298.15$ K; *, Yamamoto et al.[6] at $T = 298.15$ K; △, Zafarani-Moattar et al.[7] at $T = 298.15$ K; —, Antoine equation.

of the vapor pressure results of $CaCl_2 + CH_3OH$ solutions with the results of Hongo et al.[5] was ± 0.92 %; with the results of Yamamoto et al.,[6] it was ± 0.99 %; and with the results of Zafarani-Moattar et al.,[7] it was ± 0.05 %. The vapor pressure results of $CaCl_2 + C_2H_5OH$ solutions were presented by Yamamoto et al.[6] at $m = (0.311$ to $1.879)$ mol·kg^{-1}. We compared our values with those from ref 6, and ± 0.43 % average deviation between two sets of results were found. The vapor pressure results of $CaCl_2 + C_2H_5OH$ solutions of Zafarani-Moattar and Jahanbir-Sardroodi[8] are presented at $m = (0.1362$ to $2.3717)$ mol·kg^{-1}. The average deviation of these results from our results was ± 0.16 %.

The activity of the solvent (a_s) and osmotic coefficients (ϕ) were calculated from the experimental vapor pressure values using the following equations:

$$\ln a_s = \ln(p/p^*) + (B_s - V_s^*)(p - p^*)/RT \qquad (1)$$

$$\phi = -\ln a_s/(\nu m M_s) \qquad (2)$$

The parameters of eqs 1 and 2 (the values of p^*, B_s, and V_s^*) for both solvents were presented in refs 9 and 10. The obtained values of activity of the solvent (a_s) and osmotic coefficients (ϕ) are tabulated in Table 3.

The experimental vapor pressure results of the investigated solutions were fitted to the Antoine equation:

$$\ln p = A - B/(T + C) \qquad (3)$$

Table 3. Calculated Activity of Solvent a_s and Osmotic Coefficients ϕ of the Investigated Solutions

m/(mol·kg^{-1})	a_s	ϕ	a_s	ϕ	a_s	ϕ
			$CaCl_2 + CH_3OH$			
	T = 298.15 K		T = 303.15 K		T = 308.15 K	
0.10402	0.993669	0.635	0.993801	0.622	0.993862	0.616
0.18097	0.989312	0.618	0.989622	0.600	0.989828	0.588
0.30129	0.982863	0.597	0.983331	0.580	0.983899	0.560
0.34007	0.980655	0.598	0.981353	0.576	0.981899	0.559
0.37895	0.978563	0.595	0.979241	0.576	0.979933	0.556
0.56187	0.967577	0.610	0.968766	0.588	0.969964	0.565
0.65834	0.961356	0.623	0.962829	0.599	0.964346	0.574
1.02825	0.931397	0.719	0.933715	0.694	0.936236	0.667
1.08516	0.926217	0.735	0.928447	0.712	0.931067	0.685
1.23112	0.912185	0.777	0.91498	0.751	0.917384	0.729
1.42494	0.891506	0.838	0.893933	0.819	0.896617	0.797
1.86317	0.840128	0.973	0.843753	0.949	0.847235	0.926
2.45128	0.765746	1.133	0.769542	1.112	0.773386	1.091
2.59613	0.747958	1.164	0.75097	1.148	0.755119	1.126
	T = 313.15 K		T = 318.15 K		T = 323.15 K	
0.10402	0.993985	0.603	0.994088	0.593	0.994194	0.582
0.18097	0.990149	0.569	0.990364	0.557	0.990591	0.543
0.30129	0.984491	0.540	0.984887	0.526	0.98543	0.507
0.34007	0.982559	0.538	0.983156	0.520	0.983697	0.503
0.37895	0.980736	0.534	0.981491	0.513	0.98214	0.495
0.56187	0.971485	0.536	0.972855	0.510	0.974262	0.483
0.65834	0.966125	0.545	0.967768	0.518	0.969306	0.493
1.02825	0.938839	0.639	0.941346	0.612	0.943206	0.592
1.08516	0.933997	0.655	0.936338	0.631	0.938785	0.606
1.23112	0.919992	0.705	0.922825	0.679	0.925673	0.653
1.42494	0.900824	0.763	0.903912	0.738	0.907261	0.711
1.86317	0.851027	0.901	0.855623	0.871	0.85917	0.848
2.45128	0.777777	1.067	0.782745	1.040	0.786818	1.018
2.59613	0.759462	1.103	0.765358	1.072	0.768222	1.057
			$CaCl_2 + C_2H_5OH$			
	T = 298.15 K		T = 303.15 K		T = 308.15 K	
0.12359	0.992679	0.430	0.992789	0.424	0.992867	0.419
0.21856	0.988261	0.391	0.988424	0.385	0.988616	0.379
0.43590	0.976394	0.397	0.976845	0.389	0.977301	0.381
0.63208	0.964905	0.409	0.965455	0.402	0.966201	0.394
0.89583	0.947731	0.434	0.948841	0.424	0.949908	0.415
1.14832	0.929669	0.460	0.931274	0.449	0.932600	0.440
1.44645	0.905792	0.495	0.907812	0.484	0.909443	0.475
1.81882	0.870911	0.550	0.873128	0.540	0.875304	0.530
2.12091	0.838799	0.600	0.840994	0.591	0.843746	0.580
	T = 313.15 K		T = 318.15 K		T = 323.15 K	
0.12359	0.992922	0.416	0.993016	0.410	0.993105	0.405
0.21856	0.988718	0.376	0.988901	0.369	0.989087	0.363
0.43590	0.977655	0.375	0.978143	0.367	0.978573	0.360
0.63208	0.966866	0.386	0.967467	0.379	0.96829	0.369
0.89583	0.950651	0.409	0.951857	0.399	0.95301	0.389
1.14832	0.933655	0.433	0.934995	0.424	0.93645	0.414
1.44645	0.910948	0.467	0.912761	0.457	0.914414	0.448
1.81882	0.877534	0.520	0.879774	0.510	0.881989	0.500
2.12091	0.846482	0.569	0.849212	0.558	0.852223	0.546

Table 4. Constants of the Antoine Equation $\ln(p/\mathrm{Pa}) = A - B/(T/\mathrm{K} + C)$ and Standard Percent Deviations of the Investigated Solutions

m / mol·kg^{-1}	A	B	C	$\delta p/p$ / %
		$CaCl_2 + CH_3OH$		
0.10402	23.8674	3852.81	−25.5824	0.021
0.18097	23.8549	3845.63	−25.9357	0.022
0.30129	23.8767	3857.33	−25.6560	0.021
0.34007	23.8681	3852.10	−25.9033	0.021
0.37895	23.9234	3882.83	−24.8422	0.020
0.56187	24.0887	3972.92	−21.9367	0.022
0.65834	24.0729	3962.84	−22.4606	0.020
1.02825	23.9273	3882.46	−25.9053	0.015
1.08516	24.0848	3973.12	−22.7011	0.019
1.23112	24.2026	4047.81	−20.0881	0.026
1.42494	24.5162	4233.56	−13.9133	0.032
1.86317	24.4323	4204.28	−15.4231	0.014
2.45128	24.5956	4342.36	−11.1021	0.017
2.59613	24.6546	4391.03	−9.4714	0.050
		$CaCl_2 + C_2H_5OH$		
0.12359	23.6023	3692.44	−45.8972	0.015
0.21856	23.6752	3729.41	−44.7097	0.016
0.43590	23.6940	3735.54	−44.8273	0.015
0.63208	23.7237	3747.64	−44.7270	0.019
0.89583	23.6254	3692.22	−47.1133	0.018
1.14832	23.8101	3788.86	−44.0578	0.018
1.44645	23.7492	3756.18	−45.6599	0.019
1.81882	23.6935	3723.24	−47.6069	0.017
2.12091	23.5605	3648.99	−51.0334	0.031

The evaluated constants A, B, and C for the investigated solutions are tabulated in Table 4. The standard mean percent deviation is given by

$$\delta p/p\ (\%) = \left(\frac{\sum_{i=1}^{n} (p_{\mathrm{exp}} - p_{\mathrm{cal}})/p_{\mathrm{exp}}}{n} \right) \times 100 \qquad (4)$$

The Antoine equation fits our experimental results with standard deviation of less than ± 0.019 % for the $CaCl_2 + CH_3OH$ and ± 0.012 % for the $CaCl_2 + C_2H_5OH$ solutions. The average absolute deviation Δ_{AAD}, bias Δ_{Bias}, root-mean-square deviation Δ_{RMS}, standard deviation Δ_{STD}, and maximum absolute deviation Δ_{Max} were calculated using the following equations:

$$\Delta_{\mathrm{AAD}}/\mathrm{Pa} = \frac{\sum_{i=1}^{n} |p_{\mathrm{exp}} - p_{\mathrm{cal}}|}{n} \qquad (5)$$

$$\Delta_{\mathrm{Bias}}/\mathrm{Pa} = \frac{\sum_{i=1}^{n} (p_{\mathrm{exp}} - p_{\mathrm{cal}})}{n} \qquad (6)$$

$$\Delta_{\mathrm{RMS}}/\mathrm{Pa} = \left[\frac{\sum_{i=1}^{n} (p_{\mathrm{exp}} - p_{\mathrm{cal}})^2}{n} \right]^{1/2} \qquad (7)$$

$$\Delta_{\mathrm{STD}}/\mathrm{Pa} = \sqrt{\frac{\sum_{i=1}^{n} (p_{\mathrm{exp}} - p_{\mathrm{cal}})^2}{n(n-1)}} \qquad (8)$$

$$\Delta_{\mathrm{Max}}/\mathrm{Pa} = \max|p_{\mathrm{exp}} - p_{\mathrm{cal}}| \qquad (9)$$

where p_{cal} is the vapor pressure calculated from an Antoine equation and n is the number of experimental points considered. The deviations were for the $CaCl_2 + CH_3OH$ solutions: Δ_{AAD} = 6.155 Pa, Δ_{Bias} = 0.356 Pa, Δ_{RMS} = 9.370 Pa, Δ_{STD} = 1.201 Pa, Δ_{Max} = 27.721 Pa and for the $CaCl_2 + C_2H_5OH$ solutions: Δ_{AAD} = 3.423 Pa, Δ_{Bias} = 0.126 Pa, Δ_{RMS} = 4.533 Pa, Δ_{STD} = 0.623 Pa, Δ_{Max} = 12.111 Pa, respectively.

Table 5. Parameters for the Pitzer−Mayorga Model of the Investigated Solutions[a]

T/K	m/mol·kg^{-1}	A_ϕ/kg$^{1/2}$·mol$^{-1/2}$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C	$s(\phi)$
			$CaCl_2 + CH_3OH$				
298.15	0.10402 to 2.59613	1.29430	0.581407	8.819294	−4.480378	−0.036800	0.004
303.15	0.10402 to 2.59613	1.31502	0.586744	9.012059	−4.720061	−0.037368	0.004
308.15	0.10402 to 2.59613	1.33639	0.642396	10.52050	−5.854351	−0.046334	0.003
313.15	0.10402 to 2.59613	1.35832	0.639884	10.84376	−6.167041	−0.045435	0.003
318.15	0.10402 to 2.59613	1.38074	0.651690	11.35983	−6.603508	−0.047835	0.004
323.15	0.10402 to 2.59613	1.40356	0.654333	11.65454	−6.892988	−0.047990	0.005
			$CaCl_2 + C_2H_5OH$				
298.15	0.12359 to 2.12091	2.00527	0.406514	6.315487	−0.713057	−0.022114	0.006
303.15	0.12359 to 2.12091	2.04555	0.416036	6.762805	−0.844427	−0.022678	0.007
308.15	0.12359 to 2.12091	2.08720	0.468627	7.820267	−1.464017	−0.031963	0.007
313.15	0.12359 to 2.12091	2.13077	0.472306	8.243073	−1.495554	−0.031310	0.007
318.15	0.12359 to 2.12091	2.17629	0.493980	8.837304	−1.725356	−0.034238	0.008
323.15	0.12359 to 2.12091	2.22424	0.523688	9.708257	−2.119328	−0.038232	0.008

[a] $b = 3.2$ kg$^{1/2}$·mol$^{-1/2}$; $\alpha_1 = 2$ kg$^{1/2}$·mol$^{-1/2}$, $\alpha_2 = 1.4$ kg$^{1/2}$·mol$^{-1/2}$.

The experimental osmotic coefficient ϕ data were correlated with the model of Pitzer and Mayorga.[11] This model for the 2:1 electrolytes has the following form:

$$\phi - 1 = 2 f^{\phi} + (4/3)mB^{\phi}_{\mathrm{MX}} + m^2\frac{2^{5/2}}{3}C^{\phi}_{\mathrm{MX}} \tag{10}$$

where

$$f^{\phi} = -A_{\phi}(I)^{1/2}/(1 + b(I)^{1/2}) \tag{11}$$

$$A_{\phi} = (1/3)(2\pi N_{\mathrm{A}} d_{\mathrm{s}})^{1/2}[e^2/(4\pi\epsilon_0\epsilon_{\mathrm{r}}kT)]^{3/2} \tag{12}$$

and

$$B^{\phi}_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \beta^{(1)}_{\mathrm{MX}} \exp[-\alpha_{(1)}(I)^{1/2}] \tag{13}$$

For some data on aqueous and nonaqueous electrolyte solutions, it was found that, by adding a $\beta^{(2)}_{\mathrm{MX}}$ term to eq 13, better agreement with the experimental results can be obtained with the Pitzer and Mayorga model[11−13] given by

$$B^{\phi}_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \beta^{(1)}_{\mathrm{MX}} \exp[-\alpha_{(1)}(I)^{1/2}] + \beta^{(2)}_{\mathrm{MX}} \exp[-\alpha_{(2)}(I)^{1/2}] \tag{14}$$

In eqs 10 to 14, $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$, $\beta^{(2)}_{\mathrm{MX}}$, and C^{ϕ}_{MX} are Pitzer's ionic interaction parameters; $\alpha_{(1)}$, $\alpha_{(2)}$, and b are adjustable parameters. The parameters of eq 12 were discussed in ref 9. The term I is the ionic strength on a molality basis:

$$I = 0.5\sum m_j z_j^2 \tag{15}$$

where m_j is the molality of jth ion and z_j is the absolute value for the jth ionic charge. The remaining symbols have their usual meaning. For the 2:1 electrolytes, $I = 3m$.

From the analysis of the experimental osmotic coefficient data, we found that the values of adjustable parameters as $b = 3.2$ kg$^{1/2}$·mol$^{-1/2}$, $\alpha_1 = 2$ kg$^{1/2}$·mol$^{-1/2}$, and $\alpha_2 = 1.4$ kg$^{1/2}$·mol$^{-1/2}$ proposed in the literature[7,8] for the methanol and ethanol solutions of $CaCl_2$ were satisfactory for the calculations. The values of b and α_1 were recommended by Barthel et al.[14] for methanol and ethanol electrolyte solutions in correlations with the Pitzer−Mayorga equation. Ion interaction parameters obtained from fitting of experimental osmotic coefficient data for the investigated solutions are shown in Table 5 together with the Debye−Hückel limiting law slope for the osmotic coefficient in molality A_ϕ/(kg$^{1/2}$·mol$^{-1/2}$) of pure solvent and standard deviation obtained for the osmotic coefficients. The calculated osmotic coefficients ϕ against molality m of $CaCl_2$ are shown in Figures 3 and 4 together the results of the Pitzer−Mayorga model.

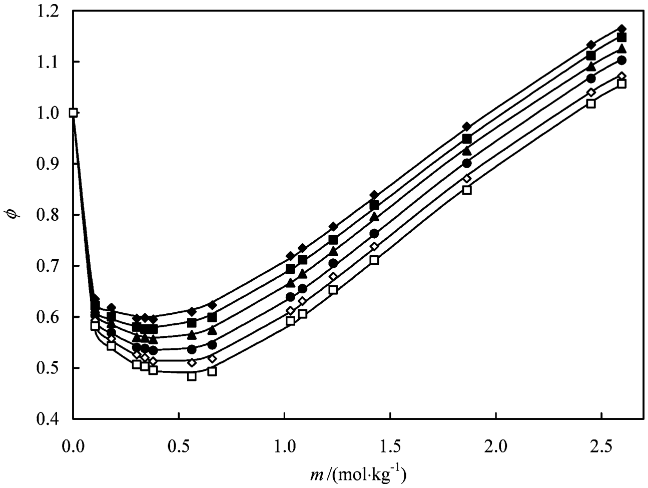

Figure 3. Osmotic coefficients ϕ of $CaCl_2 + CH_3OH$ solutions vs molality m of $CaCl_2$: ◆, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ●, 313.15 K; ◇, 318.15 K; □, 323.15 K; —, Pitzer-Mayorga model.

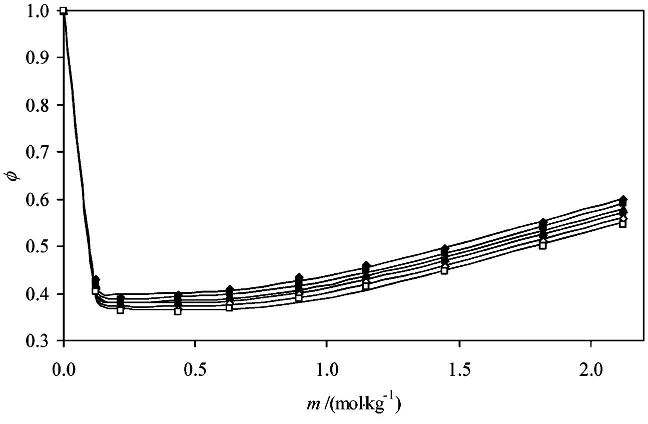

Figure 4. Osmotic coefficients ϕ of $CaCl_2 + C_2H_5OH$ solutions vs molality m of $CaCl_2$: ◆, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ●, 313.15 K; ◇, 318.15 K; □, 323.15 K; —, Pitzer-Mayorga model.

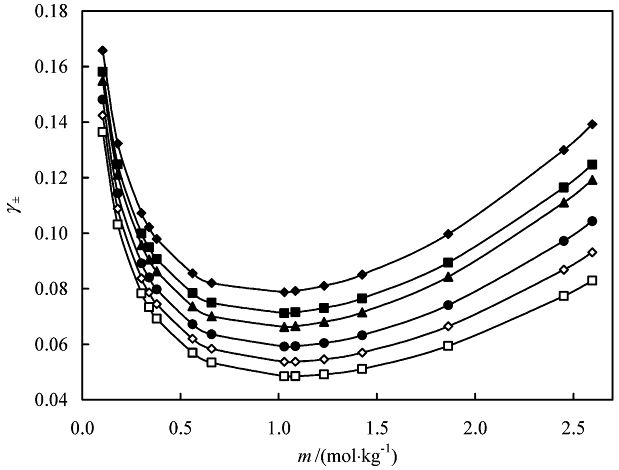

Figure 5. Mean activity coefficients $\gamma_\pm$ of $CaCl_2$ in methanol vs molality m of $CaCl_2$: ◆, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ●, 313.15 K; ◇, 318.15 K; □, 323.15 K.

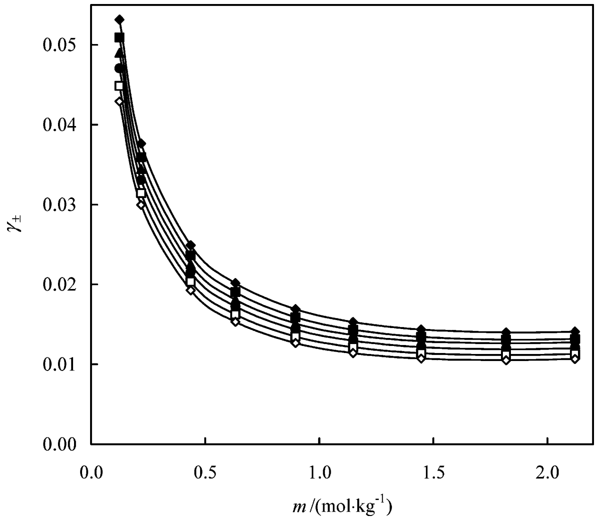

Figure 6. Mean activity coefficients $\gamma_\pm$ of $CaCl_2$ in ethanol vs molality m of $CaCl_2$: ◆, 298.15 K; ■, 303.15 K; ▲, 308.15 K; ●, 313.15 K; ◇, 318.15 K; □, 323.15 K.

The mean molal activity coefficient of $CaCl_2$ in solution $\gamma_\pm$ was calculated using the Pitzer equation[11] and presented in Table 6. The equation used for the 2:1 electrolytes is given by

$$\ln \gamma_\pm = 2f^\gamma + (4/3)mB^\gamma_{MX} + m^2(2^{5/2}/3)C^\gamma_{MX} \tag{16}$$

where

$$f^\gamma = -A_\phi[I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})] \tag{17}$$

$$B^\gamma_{MX} = 2\beta^{(0)}_{MX} + A_1 + A_2 \tag{18}$$

$$C^\gamma_{MX} = (3/2)C^\phi_{MX} \tag{19}$$

where

$$A_1 = (2\beta^{(1)}_{MX}/\alpha^2_{(1)}I)[1 - \exp(-\alpha_{(1)}I^{1/2})(1 + \alpha_{(1)}I^{1/2} - \alpha^2_{(1)}I/2)] \tag{20}$$

$$A_2 = (2\beta^{(2)}_{MX}/\alpha^2_{(2)}I)[1 - \exp(-\alpha_{(2)}I^{1/2})(1 + \alpha_{(2)}I^{1/2} - \alpha^2_{(2)}I/2)] \tag{21}$$

The validity of the mean molal activity coefficient of $CaCl_2$ in solution $\gamma_\pm$ calculations depends on how well the model describes the osmotic coefficients ϕ in the dilute region. The activity coefficient $\gamma_\pm$ values of the investigated systems from the Pitzer−Mayorga model are shown in Figures 5 and 6.

Table 6. Mean Molal Activity Coefficient $\gamma_\pm$ of $CaCl_2$ in Solvents Calculated from the Pitzer−Mayorga Model

m/ (mol·kg^{-1})	$\gamma_\pm$ T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15 K	T = 323.15 K
			$CaCl_2 + CH_3OH$			
0.10402	0.16581	0.15820	0.15487	0.14815	0.14241	0.13644
0.18097	0.13230	0.12480	0.12108	0.11444	0.10884	0.10314
0.30129	0.10724	0.09994	0.09568	0.08916	0.08373	0.07835
0.34007	0.10216	0.09491	0.09053	0.08404	0.07865	0.07336
0.37895	0.09794	0.09074	0.08625	0.07978	0.07444	0.06922
0.56187	0.08551	0.07842	0.07364	0.06719	0.06195	0.05696
0.65834	0.08205	0.07495	0.07008	0.06359	0.05835	0.05340
1.02825	0.07874	0.07122	0.06622	0.05916	0.05364	0.04848
1.08516	0.07916	0.07153	0.06651	0.05932	0.05371	0.04849
1.23112	0.08104	0.07307	0.06803	0.06043	0.05457	0.04912
1.42494	0.08508	0.07655	0.07148	0.06324	0.05695	0.05110
1.86317	0.09969	0.08945	0.08431	0.07411	0.06646	0.05938
2.45128	0.12996	0.11645	0.11105	0.09723	0.08685	0.07738
2.59613	0.13924	0.12475	0.11922	0.10433	0.09311	0.08292
			$CaCl_2 + C_2H_5OH$			
0.12359	0.05316	0.05092	0.04900	0.04707	0.04487	0.04291
0.21856	0.03765	0.03594	0.03446	0.03307	0.03142	0.02995
0.43590	0.02491	0.02364	0.02252	0.02155	0.02035	0.01928
0.63208	0.02016	0.01905	0.01810	0.01726	0.01625	0.01532
0.89583	0.01691	0.0159	0.01512	0.01436	0.01348	0.01267
1.14832	0.01530	0.01435	0.01369	0.01296	0.01215	0.01141
1.44645	0.01436	0.01344	0.01289	0.01216	0.01140	0.01072
1.81882	0.01399	0.01308	0.01263	0.01189	0.01116	0.01052
2.12091	0.01409	0.01317	0.01277	0.01202	0.01129	0.01067

Conclusions

Experimental vapor pressure data were reported for $CaCl_2 + CH_3OH$ solutions in molality range m = (0.10402 to 2.59613) mol·kg^{-1} and for $CaCl_2 + C_2H_5OH$ solutions in molality range m = (0.12359 to 2.12091) mol·kg^{-1} at T = (298.15 to 323.15) K. Experimental vapor pressure data are satisfactorily correlated using the Antoine equation. Experimental osmotic coefficients are correlated using the extended Pitzer−Mayorga model. The parameters of the Pitzer−Mayorga model were used to calculate the mean molal activity coefficient of $CaCl_2$ in solution. For the Pitzer−Mayorga model, data analysis shows that the values $b = 3.2$, $\alpha_1 = 2$, and $\alpha_2 = 1.4$ give the best overall results for the investigated systems. For this model, the $\beta^{(2)}$ parameter, which is related to the second virial coefficient, is negative. This shows the existence of ion association in these systems.

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