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$Ca(NO_3)_2$ (aq) AS HEAT TRANSFER FLUID FOR THE ALTERNATIVE ENERGY RESOURCES. II. APPARENT MOLAR VOLUMES V_ϕ

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Apparent molar volumes V_ϕ of $Ca(NO_3)_2$ (aq) at T=(298.15 to 398.15) K, at pressures up to p=60 MPa were reported, and apparent molar volumes at infinite dilution have been evaluated. An empirical correlation for partial molar volumes of calcium nitrate in water with pressure, temperature and molality has been derived. The calculations were carried out at molalities m=(0.18848, 0.32075, 0.52994, 1.07546, 2.03143, and 3.28155) mol·kg^{-1} of calcium nitrate.

1. Introduction

The absorption cycle is a process by which a refrigeration effect is produced by the use of two phases of fluids and some quantity of heat input, rather than electrical input as in the more familiar vapor compression cycle and used as alternative energy resources. For the analysis of detailed properties of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers it is necessary to know the thermodynamic properties of refrigeration agents and heat transfer rates of these installations [1]. Solutions for absorption refrigerating machines and absorption heat pumps widely apply various anticorrosive and anticristallisation additivities, such as calcium nitrate [2]. In this case, it is interesting to study the thermodynamic properties of $Ca(NO_3)_2$ (aq) for the understanding of properties of them as anticorrosive and anticristallisation additivities in the absorption cycle.

This paper is a continuation of our previous publication [3] of the investigation of thermodynamic properties of $Ca(NO_3)_2$ (aq). In the present paper, the apparent molar volumes V_ϕ of $Ca(NO_3)_2$ (aq) at T=(298.15 to 398.15) K, at pressures up to p=60 MPa are reported, and apparent molar volumes at infinite dilution have been evaluated. An empirical correlation for apparent molar volumes of calcium chloride in water solutions with pressure, temperature and molality has been derived.

2. Results and discussion

The apparent molar volumes V_ϕ of the calcium nitrate in the water were defined by equation (1) and are listed in Table 1:

$$V_\varphi = 1000(\rho_w - \rho_s)/(m\rho_s\rho_w) + M/\rho_s, \quad (1)$$

where: ρ_w and ρ_s are densities of the water and solution, g/cm^3 and m is the molality of solution, mol·kg^{-1}, and M is the molar mass of the dissolved $Ca(NO_3)_2$, in g/mol.

The uncertainty in derived values of V_ϕ depends strongly on m, ρ_w and ρ_s. The maximum relative uncertainty δV_ϕ in the apparent molar volume V_ϕ determination can be estimated by the following equation [4]:

$$\delta V_\phi = \left(1 - \frac{Mm}{1000}\right)\left(\frac{\rho_w}{\rho_w - \rho_s}\right)\delta\rho_s + \left(\frac{\rho_s}{\rho_w - \rho_s}\right)\delta\rho_w + \delta m, \quad (2)$$

where: δV_ϕ is the uncertainties in the apparent molar volumes, $\delta\rho_w$=0.001% is the uncertainties in the pure water density (by the IAPWS standard), $\delta\rho_s$=0.03% is the

TABLE 1: Calculated apparent molar volumes V_ϕ/(cm^3·mol^{-1}) of $Ca(NO_3)_2$ (aq)

	m/mol·kg^{-1}					
T/K	0.18848	0.32075	0.52994	1.07546	2.03143	3.28155
			p=0.1 MPa			
298.15	43.190	43.794	44.836	46.789	49.626	52.906
323.15	47.482	47.901	48.499	49.881	52.155	54.929
348.15	48.789	49.230	49.820	51.322	53.579	56.257
373.15	48.782	49.333	50.036	51.568	54.008	56.762
			p=5 MPa			
298.15	43.411	44.105	45.112	47.013	49.788	53.017
323.15	47.575	48.010	48.595	49.970	52.263	55.019
348.15	48.833	49.315	49.884	51.379	53.640	56.304
373.15	48.893	49.396	50.129	51.653	54.100	56.799
398.15	46.818	47.623	48.619	50.559	53.368	56.465
			p=10 MPa			
298.15	43.590	44.327	45.353	47.238	50.004	53.160
323.15	47.668	48.089	48.691	50.076	52.366	55.130
348.15	48.928	49.363	49.944	51.423	53.698	56.360
373.15	49.004	49.458	50.182	51.726	54.167	56.842
398.15	47.081	47.853	48.782	50.706	53.485	56.534
			p=20 MPa			
298.15	43.791	44.568	45.563	47.471	50.218	53.333
323.15	47.793	48.178	48.784	50.158	52.467	55.251
348.15	49.002	49.454	50.019	51.469	53.772	56.431
373.15	49.102	49.539	50.239	51.781	54.227	56.890
398.15	47.355	48.058	48.931	50.872	53.589	56.601
			p=30 MPa			
298.15	44.048	44.832	45.785	47.647	50.431	53.529
323.15	47.860	48.291	48.888	50.261	52.567	55.380
348.15	49.066	49.534	50.104	51.552	53.824	56.491
373.15	49.189	49.642	50.326	51.854	54.288	56.949
398.15	47.496	48.212	49.064	51.004	53.732	56.657
			p=40 MPa			
298.15	44.260	45.025	45.996	47.823	50.618	53.679
323.15	47.964	48.390	48.961	50.369	52.671	55.480
348.15	49.175	49.637	50.180	51.619	53.898	56.540
373.15	49.264	49.735	50.421	51.928	54.371	56.996
398.15	47.677	48.316	49.242	51.132	53.843	56.714
			p=50 MPa			
298.15	44.490	45.207	46.178	48.013	50.766	53.805
323.15	48.065	48.456	49.068	50.457	52.750	55.560
348.15	49.275	49.731	50.249	51.678	53.948	56.590
373.15	49.384	49.816	50.506	52.002	54.441	57.035
398.15	47.787	48.474	49.367	51.258	53.984	56.761
			p=60 MPa			
298.15	44.701	45.414	46.374	48.200	50.894	53.940
323.15	48.106	48.543	49.148	50.537	52.840	55.630
348.15	49.366	49.786	50.328	51.766	54.001	56.640
373.15	49.439	49.920	50.562	52.077	54.499	57.069
398.15	47.884	48.585	49.499	51.373	54.091	56.810

uncertainties in the solution density, and δm=0.75% (at low concentrations) and 0.065% (at high concentrations) are the uncertainties in the concentration, respectively. The absolute average uncertainties of δV_ϕ by the investigated concentrations are: δV_ϕ= (1.3707, 0.79668, 0.47305, 0.21983, 0.10198 and 0.0489) %, respectively.

The calculated values of apparent molar volumes V_ϕ of $Ca(NO_3)_2$ (aq) were compared with literature values. The results of these comparisons at T=298.15 K and p=0.1 MPa are shown in Figure 1. Figure 2 shows the plot of apparent molar volume V_ϕ of $Ca(NO_3)_2$ (aq) against temperature T at m=0.52994 mol·kg^{-1}.

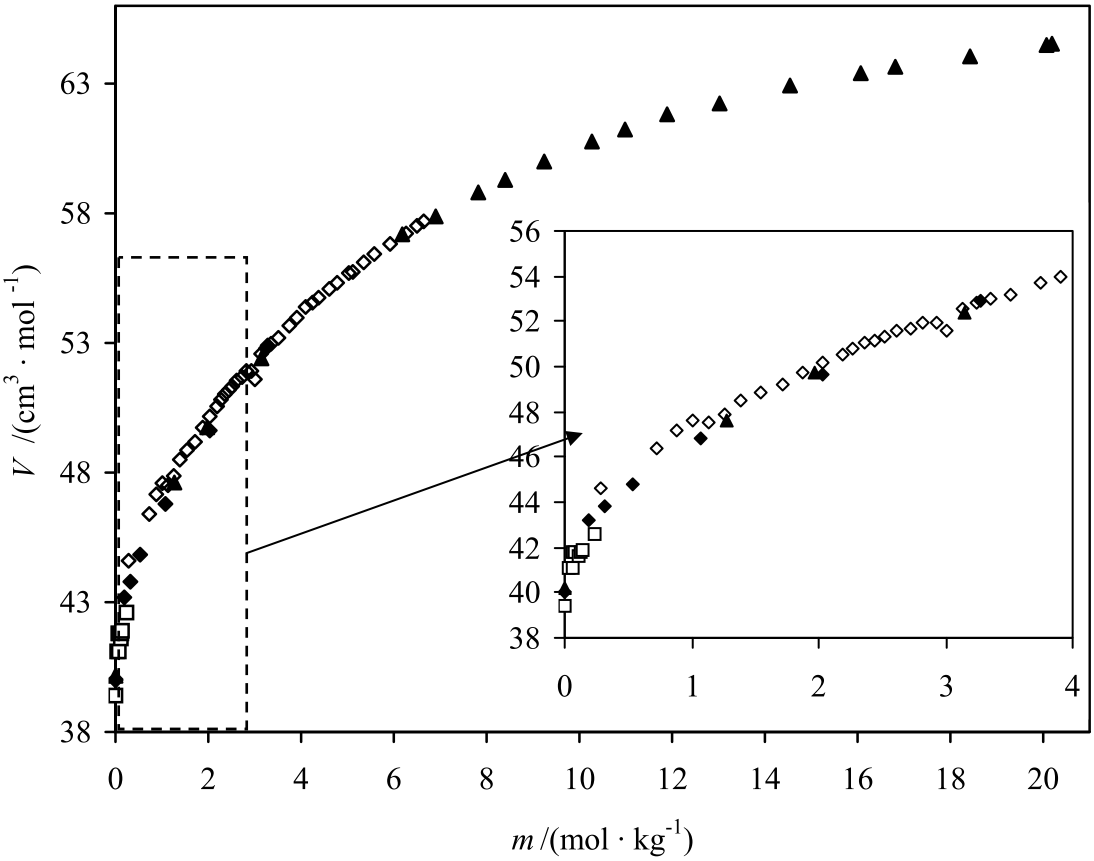

FIGURE 1. Plot of apparent molar volume V_ϕ of $Ca(NO_3)_2$ (aq) against molalities m at T=298.15 K and p=0.1 MPa, together with values reported in the literature (◆, this work; ▲, Ewing and Mikovsky [5]; □, Spitzer *etc.* [6]; ◇, Vercher *etc.* [7]).

The apparent molar volume of calcium nitrate at infinite dilution V_ϕ^0 at constant temperature T and pressure p can be evaluated from the following equation:

$$V_\phi = V_\phi^0 + A_v m^{1/2} + B_v m\,, \qquad (3)$$

where: V_ϕ^0 is the apparent molar volume of calcium nitrate at infinite dilution, which is the same as the partial molar volume of calcium nitrate at infinite dilution, A_v is the Debye-Hückel limiting slope, m is the molality, and B_v is an adjustable parameter.

Redlich *etc.* [8-9] attempted to prove the Masson hypothesis for deriving of A_v by using Debye-Hückel theory [10]:

$$A_v = kw^{3/2} \qquad (4)$$

Archer and Wang [11] calculated the values of A_v for 1:1 electrolytes:

$$A_\phi = \frac{1}{3}(2\pi N_a \rho)^{1/2}[(e^2/4\pi\varepsilon_0\varepsilon_r kT)]^{3/2}\,, \qquad (5)$$

$$k_v = -4RT(\partial A_\phi/\partial p)_T = 6RTA_\phi[(\partial \ln\varepsilon_r/dp) - \beta/3] \qquad (6)$$

where: N_A=6.02214199·10^{23} mol^{-1} is Avogadro's constant; ρ is the density, kg/m^3; β is the isothermal compressibility, MPa^{-1} and ε_r is the relative permitivity; e=1.6021773·10^{-19} C is the charge of electron; ε_0=8.8541878·10^{-12} F·m^{-1} is the permittivity of vacuum; k=1.3806503·10^{-23} J·K^{-1} is the Boltzmann constant; T is the absolute temperature, K; R=8.31441 J·mol^{-1}·K^{-1} is the universal gas constant; A_ϕ is Pitzer-Debye-Hückel limiting slope for the osmotic coefficient, $kg^{1/2}$·$mol^{-1/2}$. w=3 were founded for 2:1 electrolytes:

$$w = 0.5\sum_i \nu_i z_i^2\,, \tag{7}$$

where: ν_i is the number of ions of species i and valency z_i formed by one molecule of electrolyte. According to (7) for an electrolyte of a fixed valence type, w is constant and the limiting slope A_v depends only on temperature and the physical properties of the solvent ε_r, $\partial \ln\varepsilon_r/\partial p$ and β. As a rule, this relationship is applied at fixed pressure p and temperature T. The infinite-dilution values of V_ϕ^0 are obtained by polynomial extrapolating Eq. (3) to zero molality of solution (m=0).

The apparent molar volumes of calcium nitrate at infinite dilution V_ϕ^0 are listed in Table 2 and the adjustable parameter B_v in Table 3. Figure 2 shows the plot of V_ϕ^0 against temperature T at m=0.52994 mol·kg^{-1}.

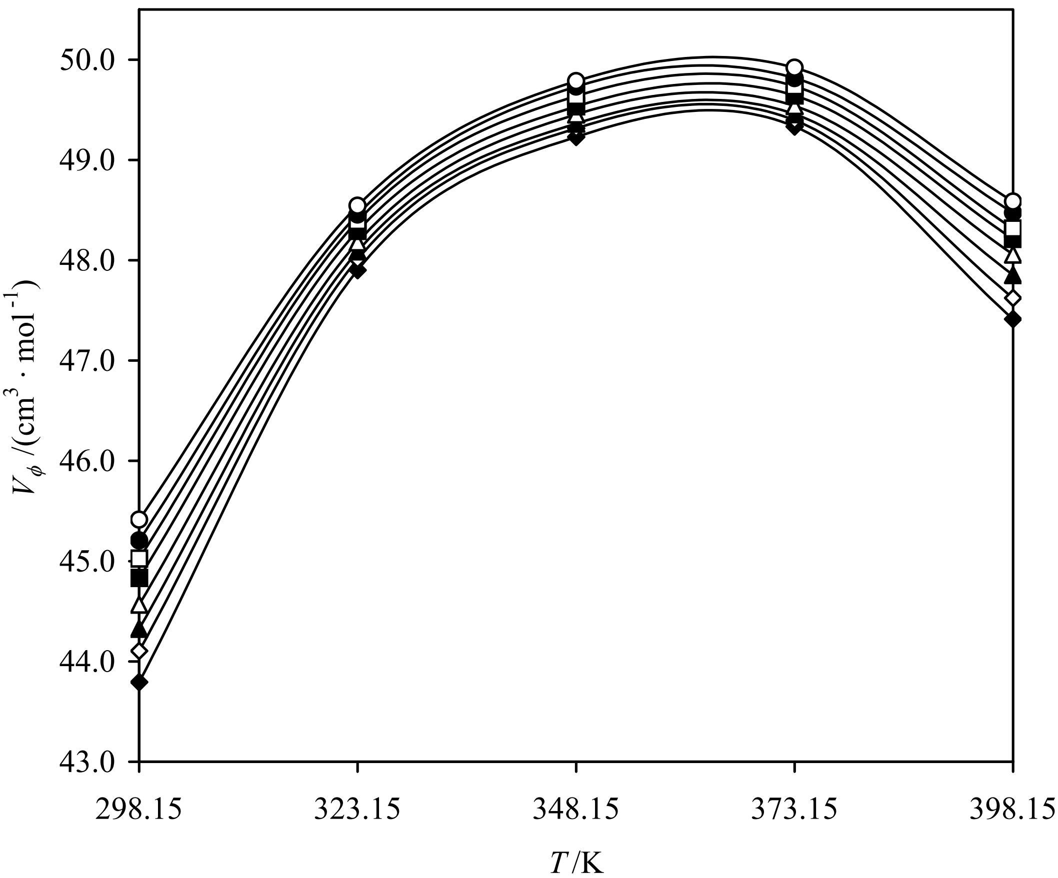

FIGURE 2. Plot of apparent molar volume V_ϕ of $Ca(NO_3)_2$ (aq) against temperature T at m=0.52994 mol·kg^{-1} (◆, 0.1 MPa; ◇, 5 MPa; ▲,10 MPa; △, 20 MPa; ■, 30 MPa; □, 40 MPa; •, 50 MPa; ○, 60 MPa).

There are several values of apparent molar volumes of $Ca(NO_3)_2$ at infinite dilution V_ϕ^0 to be found in the literatures [5, 6, 7, 12, 13, 14]. Ewing and Mikovsky [5] described the values of V_ϕ^0 at T=(298.15, 303.15, 313.15, 323.15, and 333.15) K. The comparison of the presented values with those from [5] was at T=(298.15 and 323.15) K. The ΔV_ϕ^0=0.172 $cm^3 \cdot mol^{-1}$ and ΔV_ϕ^0=2.709 $cm^3 \cdot mol^{-1}$ deviations were obtained, respectively.

TABLE 2: Apparent molar volumes at infinite dilution $V_\phi^0/(cm^3 \cdot mol^{-1})$.

T/K	p/MPa							
	0.1	5	10	20	30	40	50	60
298.15	39.992	40.105	40.243	40.426	40.709	40.982	41.313	41.561
323.15	43.871	43.982	44.134	44.385	44.456	44.631	44.842	44.874
348.15	44.205	44.259	44.489	44.665	44.823	45.047	45.255	45.490
373.15	42.741	43.033	43.323	43.649	43.899	44.118	44.449	44.578
398.15	-	38.779	39.264	39.960	40.374	40.928	41.210	41.506

TABLE 3: Apparent molar volume concentration dependence constants B_v/ $(cm^3 \cdot kg \cdot mol^{-2})$.

T/K	p/MPa							
	0.1	5	10	20	30	40	50	60
298.15	-4.9405	-4.1759	-3.7682	-3.3090	-3.1086	-3.1130	-3.3435	-3.2480
323.15	-9.0897	-8.8041	-8.7489	-8.7178	-8.0890	-7.8656	-7.8856	-7.3093
348.15	-12.7552	-12.1637	-12.2448	-11.6016	-11.0080	-10.6171	-10.2584	-10.1556
373.15	-17.2091	-17.1139	-17.0398	-16.3415	-15.4669	-14.6406	-14.3024	-13.3476
398.15	- -21.9433	-21.4802	-20.6874	-19.4045	-18.9136	-17.5743	-16.5767	

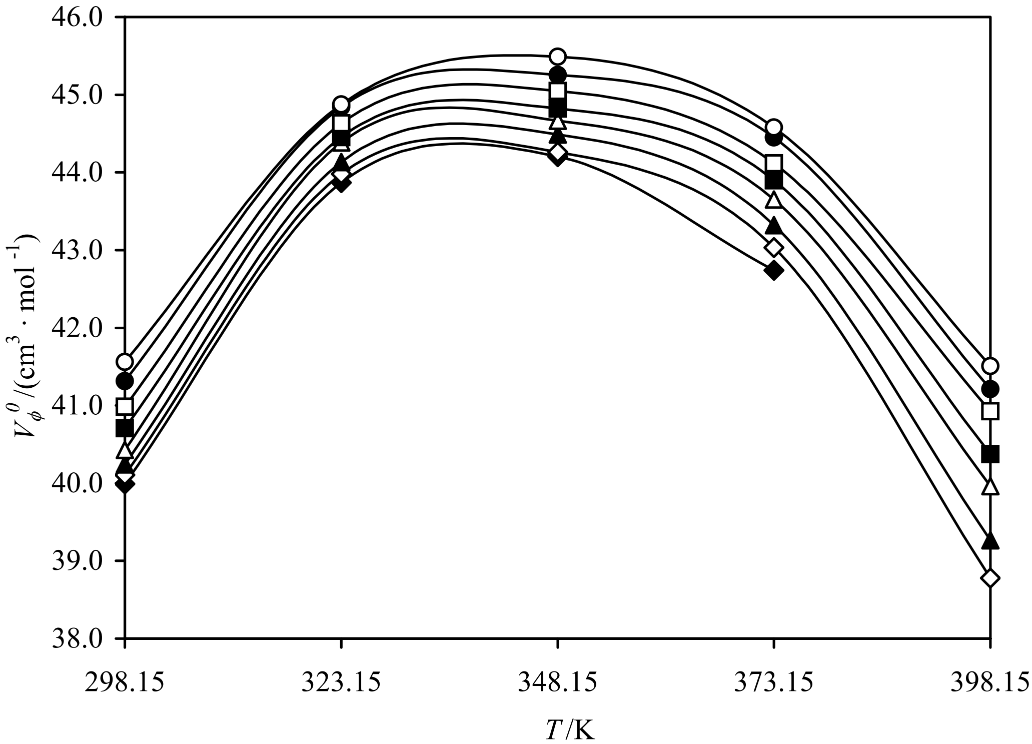

FIGURE 3. Plot of apparent molar volumes at infinite dilution V_ϕ^0 of $Ca(NO_3)_2$ (aq) against temperature T (◆, 0.1 MPa; ◇, 5 MPa; ▲, 10 MPa; △, 20 MPa; ■, 30 MPa; □, 40 MPa; •, 50 MPa; ○, 60 MPa).

The V_ϕ^0 result of Spitzer *etc.* [6] was published at T=298.15 K. The comparison of that V_ϕ^0 with our values shows a difference of ΔV_ϕ^0=-0.592 $cm^3 \cdot mol^{-1}$. The apparent molar volumes of $Ca(NO_3)_2$ at infinite dilution result of Vercher *etc.* [7] is V_ϕ^0=40.03 $cm^3 \cdot mol^{-1}$ and has ΔV_ϕ^0=0.038 $cm^3 \cdot mol^{-1}$ deviation from our results. The result of V_ϕ^0 from density of Pearce and Blackman [12] are presented at T=298.15 K. The comparison of the present values of V_ϕ^0

with them from [12] shown the ΔV_{ϕ}^{0}=-3.792 $cm^3 \cdot mol^{-1}$ average deviation. The V_{ϕ}^{0} results of Millero [13] was presented at T=298.15 K. The deviation of this value from the presented is ΔV_{ϕ}^{0}=0.158 $cm^3 \cdot mol^{-1}$. Krumgalz *etc.* [14] presented the values of V_{ϕ}^{0} calculated using ICT [15] as V_{ϕ}^{0}=40.39 $cm^3 \cdot mol^{-1}$. This value has ΔV_{ϕ}^{0}=0.398 $cm^3 \cdot mol^{-1}$ difference from our results. The results of comparison of apparent molar volumes of $Ca(NO_3)_2$ at infinite dilution V_{ϕ}^{0} with literature values at T=298.15 K and p=0.1 MPa are shown in Figure 4.

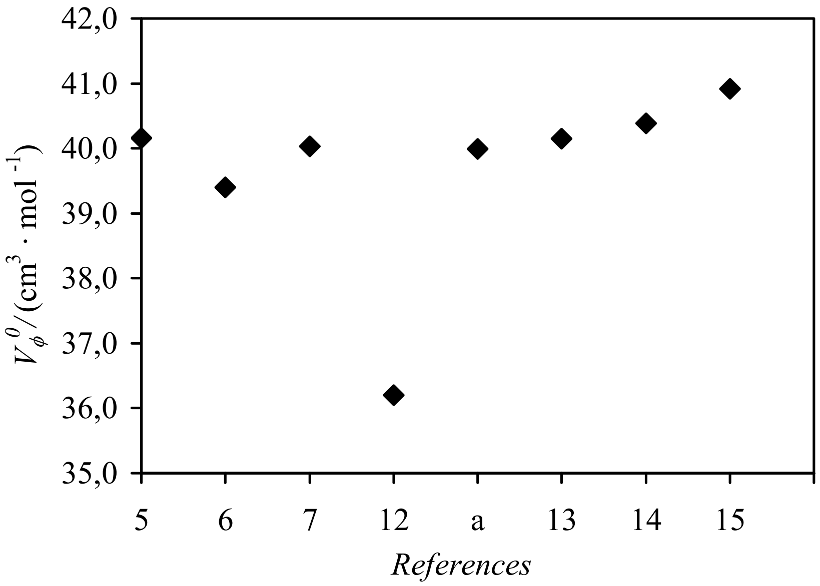

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FIGURE 4. The apparent molar volume at infinite dilution V_{ϕ}^{0} of $Ca(NO_3)_2$ (aq) at T=298.15 K, at p=0.1 MPa, together with values reported in the literature.

4. Conclusion

The apparent molar volumes V_{ϕ} of $Ca(NO_3)_2$ (aq) at T=(298.15 to 398.15) K, at pressures up to p=60 MPa are reported, and apparent molar volumes at infinite dilution V_{ϕ}^{0} have been evaluated. An empirical correlation for partial molar volumes of calcium chloride in water solutions with composition, pressure and temperature has been derived. The calculations are carried out at molalities m=(0.18848, 0.32075, 0.52994, 1.07546, 2.03143, and 3.28155) $mol \cdot kg^{-1}$ of calcium nitrate. The obtained results are compared with corresponding literature values.

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CA$(NO_3)_2$ (SULU) ALTERNATİV ENERJİ MƏNBƏƏLƏRİNDƏ İSTİFADƏ ÜÇÜN. II. V_ϕ XƏYALİ MOLYAR HƏCMİ

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$Ca(NO_3)_2$ (sulu) qarışıqlarının *T*=(298.15-dən 398.15) K və *p*=60 MPa təzyiqə qədər xəyali molyar həcmi V_ϕ təqdim olunmuş, qeyri-məhdud həllolma anında xəyali molyar həcm tapılmışdır. $Ca(NO_3)_2$-ün suda təzyiq, temperatur və molyar konsentraysiyadan asılı pasial molyar həcmi üçün empirik korrelyasiya edilmişdir. Təcrübələr m=(0.18848, 0.32075, 0.52994, 1.07546, 2.03143, və 3.28155) mol·kq^{-1} molyar konsentraysiyada aparılmışdır.

CA$(NO_3)_2$ (ВОД.) ДЛЯ ПРИМЕНЕНИЯ В АЛЬТЕРНАТИВНЫХ ИСТОЧНИКАХ ЭНЕРГИИ. II. КАЖУЩИЙСЯ МОЛЯРНЫЙ ОБЪЕМ V_ϕ

САФАРОВ Д.Т., НАДЖАФОВ Г.Н., ШАХВЕРДИЕВ А.Н., ГУСЕЙНОВ С.О., ХАССЕЛ Е.Р.

Приведены кажущийся молярный объем V_ϕ $Ca(NO_3)_2$ (вод.) и *T*=(298.15 до 398.15) K, давлениях до *p*=60 MPa, и найден кажущийся молярной объем в бесконечном разбавлении. Приведена эмпирическая корреляция парциального молярного объема кальция нитрата в воде в зависимости от давления, температуры и молярной концентрации. Эксперименты проведены при *m*=(0.18848, 0.32075, 0.52994, 1.07546, 2.03143, и 3.28155) моль·кг$^{-1}$ молярной концентрации кальция нитрата.