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Thermodynamics of complexation of aqueous 18-crown-6 with barium ion: apparent molar volumes and apparent molar heat capacities of aqueous (18-crown-6 + barium nitrate) at temperatures (278.15 to 393.15) K, at molalities (0.02 to 0.33) $mol \cdot kg^{-1}$, and at the pressure 0.35 MPa

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Abstract

We have measured the densities at T = (278.15 to 368.15) K and heat capacities at T = (278.15 to 393.15) K of aqueous solutions of {18-crown-6 + $Ba(NO_3)_2$} at molalities m = (0.02 to 0.33) $mol \cdot kg^{-1}$ and at the pressure 0.35 MPa. We have applied Young's rule and have accounted for chemical speciation and relaxation effects to resolve V_ϕ and $C_{p,\phi}$ to include contributions of the 18-crown-6–Ba^{2+}(aq) complex in the mixture. We have also calculated estimates of the change in volume $\Delta_r V_m$, the change in heat capacity $\Delta_r C_{p,m}$, the change in enthalpy $\Delta_r H_m$, and the equilibrium quotient lg Q for formation of the complex at T = (278.15 to 393.15) K and m = (0 to 0.33) $mol \cdot kg^{-1}$ in the mixture.

Keywords: Apparent molar volume; Apparent molar heat capacity; 18-Crown-6; Barium nitrate; Young's rule

1. Introduction

We recently reported the apparent molar volumes V_ϕ and apparent molar heat capacities $C_{p,\phi}$ for aqueous 18-crown-6 + KCl {(18C6 + KCl)}(aq) [1]. We have continued our investigations of the crown ether with other ions by studying the interaction of barium ion with 18C6 in water. Because of the almost identical ionic radii of Ba^{2+} and K^+, we expect the 18C6–Ba^{2+} interaction to be stronger than that for 18C6–K^+ due to the increased nuclear charge of Ba^{2+}. We report here experimental values of V_ϕ at T = (278.15 to 368.15) K and $C_{p,\phi}$ at T = (278.15 to 393.15) K for {18C6 + $Ba(NO_3)_2$}(aq) at molalities m = (0.02 to 0.33) $mol \cdot kg^{-1}$ and at the pressure 0.35 MPa. We applied Young's rule to the results for {18C6 + $Ba(NO_3)_2$}(aq) and accounted for chemical relaxation effects to resolve V_ϕ and $C_{p,\phi}$ to include contributions of the complex 18C6–Ba^{2+}(aq). As with our previous work with (18C6–K^+, Cl^-)(aq) [1], we are also the first to report $C_{p,\phi}$ for (18C6–Ba^{2+}, $2NO_3^-$)(aq). We have again calculated estimates of the change in volume, $\Delta_r V_m$, the change in heat capacity, $\Delta_r C_{p,m}$, the change in enthalpy, $\Delta_r H_m$, and the equilibrium quotient lg Q for the complexation reaction over the same ranges of T and m using values of lg K and $\Delta_r H_m^\circ$ at T = 298.15 K from the literature. The literature values of $\Delta_r H_m^\circ$ and lg K for the formation of (18C6–Ba^{2+}) in water at T = 298.15 K were abundant and

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generally showed good agreement [2–12], with the reported values of lg$K$ showing some scatter. A few investigators also reported values at other temperatures [2–4]. Values for $\Delta_r V_m$ were found only in reference [13].

2. Experimental

We used as received 18C6(c) (Sigma–Aldrich, Milwaukee, WI, USA, product 274984, lots 11630JB and 06004BI, reported purity 0.999 mass fraction, molar mass $M_2 = 264.3167\ g \cdot mol^{-1}$) and $Ba(NO_3)_2$(c) (Sigma–Aldrich, Milwaukee, WI, USA, product 202754, lot 06921TO, metal basis purity 0.99999 mass fraction, $M_2 = 261.3377\ g \cdot mol^{-1}$) to prepare aqueous solutions of $\{18C6 + Ba(NO_3)_2\}$ with $Ba(NO_3)_2$ in slight excess as noted in table 1. Other details of solution preparation are as described elsewhere [14].

Solution densities were measured using a vibrating-tube densimeter (Model DMA 512, Anton PAAR, Austria), as described previously [15]. Solution massic heat capacities were measured using a twin fixed-cell, power-compensation, differential-output, temperature-scanning calorimeter (NanoDSC 6100, Calorimetric Sciences Corporation, Lindon, UT, USA) as described previously [15]. Equations and procedures for the calculation of solution densities ρ_s, massic heat capacities $c_{p,s}$, V_ϕ, $C_{p,\phi}$, and associated uncertainties are similar to methods in a recent report [16].

3. Results and discussion

Our experimental values of V_ϕ and $C_{p,\phi}$ for the mixture $\{18\text{-crown-}6 + Ba(NO_3)_2\}(aq)$ are given in tables 1 and 2, respectively. Our results are also

TABLE 1
Observed apparent molar volumes V_ϕ for aqueous $\{18\text{-crown-}6 + Ba(NO_3)_2\}$ at $p = 0.35$ MPa[a]

m[b] / $(mol \cdot kg^{-1})$	V_ϕ / $(cm^3 \cdot mol^{-1})$	V_ϕ / $(cm^3 \cdot mol^{-1})$	V_ϕ / $(cm^3 \cdot mol^{-1})$	V_ϕ / $(cm^3 \cdot mol^{-1})$
	T = 278.15 K	T = 283.15 K	T = 288.15 K	T = 298.15 K
0.0208_4	281.6 ± 2.2	283.5 ± 2.3	284.7 ± 1.7	289.1 ± 1.4
0.0305_0	277.6 ± 3.5	281.3 ± 2.6	284.1 ± 2.6	289.3 ± 3.4
0.0418_7	278.2 ± 2.6	281.5 ± 2.0	284.2 ± 1.9	288.5 ± 2.5
0.0495_4	281.4 ± 2.9	285.2 ± 2.4	287.6 ± 2.5	291.1 ± 3.0
0.0590_4	277.5 ± 1.9	280.9 ± 1.5	283.8 ± 1.4	288.1 ± 1.8
0.0792_6	284.46 ± 0.69	285.53 ± 0.77	287.44 ± 0.71	291.25 ± 0.80
0.101_8	280.1 ± 1.2	282.8 ± 1.0	285.0 ± 1.0	288.91 ± 0.91
0.149_9	283.35 ± 0.74	286.03 ± 0.74	288.19 ± 0.76	291.64 ± 0.77
0.250_7	285.50 ± 0.68	287.79 ± 0.66	289.56 ± 0.68	292.71 ± 0.71
0.332_2	285.86 ± 0.67	288.29 ± 0.64	290.37 ± 0.67	293.32 ± 0.69
	T = 308.15 K	T = 318.15 K	T = 328.15 K	T = 338.15 K
0.0208_4	292.1 ± 1.5	294.4 ± 2.3	297.2 ± 3.3	298.4 ± 2.1
0.0305_0	293.7 ± 4.7	297.0 ± 6.8	300.0 ± 4.9	301.3 ± 4.8
0.0418_7	292.7 ± 3.5	295.9 ± 5.0	299.1 ± 3.6	300.8 ± 3.5
0.0495_4	294.6 ± 3.6	297.8 ± 4.7	300.9 ± 4.0	303.0 ± 3.9
0.0590_4	292.0 ± 2.5	295.0 ± 3.6	297.5 ± 2.6	298.9 ± 2.5
0.0792_6	294.59 ± 0.95	297.85 ± 0.94	300.2 ± 1.3	302.4 ± 1.1
0.101_8	292.3 ± 1.1	294.8 ± 1.4	297.3 ± 1.2	299.5 ± 1.3
0.149_9	294.77 ± 0.75	297.40 ± 0.72	300.10 ± 0.75	302.54 ± 0.78
0.250_7	295.50 ± 0.69	298.07 ± 0.70	300.44 ± 0.67	302.87 ± 0.68
0.332_2	296.09 ± 0.68	298.82 ± 0.69	301.28 ± 0.66	303.65 ± 0.66
	T = 348.15 K	T = 358.15 K	T = 368.15 K	
0.0208_4	299.2 ± 1.8	300.1 ± 1.5	302.38 ± 0.95	
0.0305_0	303.6 ± 3.8	302.9 ± 2.9	301.8 ± 5.0	
0.0418_7	301.9 ± 2.8	303.0 ± 2.1	303.2 ± 3.7	
0.0495_4	305.1 ± 3.7	307.5 ± 3.1	309.3 ± 3.4	
0.0590_4	300.5 ± 2.0	301.5 ± 1.6	303.7 ± 2.6	
0.0792_6	304.3 ± 1.2	305.83 ± 0.97	307.30 ± 0.72	
0.101_8	301.1 ± 1.5	302.5 ± 1.3	303.7 ± 1.3	
0.149_9	304.80 ± 0.72	306.86 ± 0.71	309.12 ± 0.64	
0.250_7	305.07 ± 0.65	307.15 ± 0.64	309.23 ± 0.66	
0.332_2	305.68 ± 0.63	307.51 ± 0.63	309.63 ± 0.64	

The ± values are from propagation of uncertainties as described in reference [16].

[a] Experimental values of ρ_s can be obtained by equation (8) with $m_t = m$, ρ_w from reference [17], and $M_{2,eq} = 525.6543\ g \cdot mol^{-1}$.

[b] Molality of 18C6. Stoichiometric molality ratios $r = m(18\text{-crown-}6)/m\{Ba(NO_3)_2\} = 0.998_4$ at $m \leqslant 0.101_8\ mol \cdot kg^{-1}$ and $r = 0.994_2$ for $m \geqslant 0.149_9\ mol \cdot kg^{-1}$.