Journal of Engineering Physics and Thermophysics, Vol. 76, No. 2, 2003

BULK PROPERTIES OF THE AQUEOUS SOLUTIONS OF BARIUM CHLORIDE

N. D. Azizov

UDC 541.135

Experimental investigations of the density of the aqueous solutions of $BaCl_2$ at temperatures of 298–573 K and pressures up to 40 MPa have been carried out with the method of a constant-volume piezometer. The error of experimental data does not exceed 0.06%. The equation of state has been composed and the coefficients of thermal expansion and isothermal compressibility and the partial molar volumes of the electrolyte have been calculated on its basis.

The aqueous solutions of alkali-earth-metal chlorides are used in practice in different branches of power engineering and the chemical industry, such as the geochemistry of ore formation, hydrothermal synthesis of crystals, and hydrometallurgy, which enables one to study their thermophysical properties. Experimental investigations and generalization of the experimental data obtained are the basic means of obtaining reliable information on the thermophysical properties. Since the middle 1970s, thermophysicists and chemists had carried out experimental investigations of the aqueous solutions of salts at high temperatures; however the error of the experimental results of the pioneering works was high. By the end of the 1990s, a certain amount of experimental material had been accumulated, but only a few binary systems (sodium and potassium chlorides and sodium sulfate) can be recognized as being fairly well investigated at present. In recent years, labor-intensive and sophisticated experimental works of scientists from the CIS countries have been uncommon in the literature.

Since the beginning of the 1980s, systematic investigations of a number of thermophysical properties of the aqueous solutions of electrolytes in a wide range of variation of temperatures, pressures, and concentrations have been carried out at the Azerbaijan Petroleum Academy ([1–6] and others).

The present work seeks to study the density of the aqueous solutions of barium chloride in a wide range of the parameters of state and to calculate the most important thermodynamic parameters.

Data on the density of the system $BaCl_2$–H_2O for a limited temperature range are available in the literature. In [7, 8], they are given only for 20–25^{o}C. In [9], investigations were carried out at 298–393 K and pressures up to 200 MPa. In [10], the values of the density are presented in a wider temperature range (288–413 K).

We carried out the investigations on a setup whose basic element was a solution-fillable piezometer of constant volume (V = 94.5 cm^3). The piezometer was placed in a liquid thermostat. Water (at room temperatures), glycerin (to 448 K), and molten saltpeter (above 423 K) were used as a thermostatting liquid. Agitators and an axial pump were used for intense circulation of the thermostatting liquid. Capillaries 0.6 mm in diameter were welded to the upper and lower points of the cylindrical piezometer; the capillaries were brought to the zone of room temperature. The lower capillary was connected to an observation window fixing the working volume of the piezometer. A U-shaped tube with mercury acting as a liquid-metal piston and separating the solution from the oil in the pressure gauge was connected to the observation window withstanding high pressure. A special valve, using which the liquid under study was discharged in the course of the experiments, was connected to the end of the upper capillary. A detailed description of the experimental setup, its schematic diagram, and the experimental procedure are given in [11, 12]. To prepare the binary system we used barium chloride of chemically pure grade and a distillate. The solution temperature was measured using a PTC-10 platinum resistance thermometer, while the pressure was measured with an MP-600 deadweight pressure-gauge tester with an accuracy rating of 0.05. The measurement error of the basic experimental quantities was $\pm$0.02 K for the temperature, $\pm$0.05% for the pressure, 0.02% for the piezometer volume, and 0.007% for the

Azerbaijan State Petroleum Academy, Baku, Azerbaijan. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 76, No. 2, pp. 182–186, March–April, 2003. Original article submitted July 10, 2002; revision submitted September 25, 2002.

TABLE 1. Density of the Aqueous Solutions of Barium Chloride at Different Pressures and Temperatures (ρ, g/cm^3; p, 10^5 Pa)

m	*p*	ρ	*p*	ρ	*p*	ρ	*p*	ρ	*p*	ρ
0.097	301.75 K		323.15 K		348.15 K		373.15 K		398.15 K	
	398.7	1.0302	387.6	1.0202	380.3	1.0074	390.3	0.9921	382.8	0.9739
	359.9	1.0285	307.3	1.0174	301.8	1.0044	310.3	0.9888	306.7	0.9706
	209.5	1.0222	205.3	1.0134	206.7	1.0005	203.5	0.9843	213.6	0.9663
	107.1	1.0181	110.4	1.0094	110.6	0.9964	102.1	0.9798	110.6	0.9613
	24.5	1.0143	53.2	1.0069	3.33	0.9931	49.2	0.9773	54.7	0.9587
	423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
	392.8	0.9548	374.6	0.9313	368.1	0.9069	–	–	–	–
	307.9	0.9505	310.9	0.9279	310.1	0.9032	198.8	0.8351	374.6	0.7827
	208.4	0.9454	219.1	0.9225	212.0	0.8971	165.7	0.8319	305.2	0.7718
	104.5	0.9399	120.4	0.9167	108.3	0.8897	104.1	0.8256	207.9	0.7574
	56.3	0.9374	56.7	0.9130	118.3	0.9243	62.4	0.8211	110.4	0.7396
0.2905	300.95 K		323.15 K		348.15 K		373.15 K		398.15 K	
	389.3	1.0639	398.2	1.0540	385.2	1.0410	380.2	1.0248	382.1	1.0073
	297.7	1.0601	308.4	1.0508	305.2	1.0378	301.1	1.0216	307.5	1.0042
	205.5	1.0565	209.3	1.0469	208.7	1.0339	204.2	1.0176	213.6	0.9997
	108.3	1.0524	103.2	1.0424	109.8	1.0300	105.2	1.0134	114.3	0.9950
	20.0	1.0485	52.1	1.0400	29.8	1.0265	52.9	1.0111	53.9	0.9922
	423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
	394.1	0.9882	385.6	0.9655	362.4	0.9399	377.2	0.8856	388.5	0.8194
	302.1	0.9836	313.2	0.9618	307.5	0.9370	317.3	0.8806	309.3	0.8096
	205.8	0.9788	215.3	0.9564	216.3	0.9310	216.9	0.8719	211.2	0.7959
	102.3	0.9736	120.4	0.9507	118.3	0.9243	120.4	0.8623	118.3	0.7800
0.571	290.55 K		323.15 K		348.15 K		373.15 K		398.15 K	
	392.4	1.1162	389.2	1.1031	388.1	1.0882	398.5	1.0737	385.2	1.0542
	302.6	1.1125	306.2	1.0992	304.8	1.0849	308.4	1.0700	301.8	1.0506
	208.7	1.1087	209.3	1.0948	207.9	1.0810	204.2	1.0658	213.2	1.0465
	110.2	1.1044	103.2	1.0900	111.4	1.0770	104.2	1.0618	113.9	1.0419
	24.5	1.1007	48.3	1.0876	31.78	1.0736	50.2	1.0597	53.9	1.0390
	423.15 K		448.15 K		473.15 K		523.15 K		573.15 K	
	394.1	1.0344	387.0	1.0126	395.0	0.9890	383.6	0.9344	374.6	0.8672
	306.1	1.0308	310.1	1.0087	315.0	0.9850	316.4	0.9292	308.5	0.8593
	204.2	1.0263	217.3	1.0036	217.7	0.9784	213.4	0.9204	216.9	0.8469
	103.2	1.0213	115.5	0.9980	113.2	0.9718	111.4	0.9112	127.9	0.8338
	52.1	1.0186	57.5	0.9946						
0.895	301.15 K		323.15 K		348.15 K		373.15 K		398.15 K	
	390.0	1.1659	386.3	1.1550	388.1	1.1406	385.1	1.1264	387.0	1.1063
	300.3	1.1623	302.1	1.1517	304.0	1.1374	319.2	1.1237	307.5	1.1029
	212.0	1.1587	204.5	1.1475	208.3	1.1336	213.1	1.1194	212.8	1.0987
	108.9	1.1546	117.2	1.1434	110.6	1.1296	103.1	1.1149	113.9	1.0940
	448.15 K		473.15 K		523.15 K		573.15 K			
	376.6	1.0642	382.1	1.0402	386.0	0.9867	382.1	0.9213		
	310.1	1.0608	308.5	1.0355	313.4	0.9810	308.5	0.9132		
	212.4	1.0555	205.5	1.0295	213.6	0.9731	207.1	0.9004		
	115.9	1.0501	111.4	1.0235	123.8	0.9653	117.3	0.8881		
	55.9	1.0467	–	–	–	–	–	–		

TABLE 2. Coefficients of the Equation of State

i	j	$p^i m^j$	a_{ij}	b_{ij}	c_{ij}	d_{ij}
0	0	1	0.995414	$1.876322 \cdot 10^{-4}$	$2.907949 \cdot 10^{-6}$	$5.328796 \cdot 10^{-19}$
1	0	p	$-4.7784 \cdot 10^{-5}$	$1.5815695 \cdot 10^{-7}$	$-1.77445 \cdot 10^{-9}$	$-1.16577 \cdot 10^{-21}$
2	0	p^2	$2.632635 \cdot 10^{-8}$	$-5.625967 \cdot 10^{-10}$	$3.10478 \cdot 10^{-12}$	$4.47998 \cdot 10^{-25}$
0	1	m	-0.1740108	$6.034458 \cdot 10^{-6}$	$-1.395854 \cdot 10^{-6}$	$-5.206558 \cdot 10^{-19}$
1	1	pm	$2.517947 \cdot 10^{-5}$	$-3.28874 \cdot 10^{-7}$	$1.952028 \cdot 10^{-9}$	$8.554 \cdot 10^{-22}$
2	1	p^2m	$-7.050 \cdot 10^{-8}$	$1.993304 \cdot 10^{-9}$	$-9.48683 \cdot 10^{-12}$	$1.2125 \cdot 10^{-24}$
0	2	m^2	$2.774768 \cdot 10^{-2}$	$3.395959 \cdot 10^{-5}$	$2.468604 \cdot 10^{-7}$	$2.233 \cdot 10^{-19}$
1	2	pm^2	$-6.298023 \cdot 10^{-6}$	$1.513065 \cdot 10^{-7}$	$-6.155852 \cdot 10^{-10}$	$-2.023698 \cdot 10^{-22}$
2	2	p^2m^2	$4.685555 \cdot 10^{-8}$	$-1.4 \cdot 10^{-9}$	$6.179577 \cdot 10^{-12}$	$-1.28636 \cdot 10^{-24}$

TABLE 3. Coefficients of Thermal Expansion at Different Temperatures and a Prescribed Concentration (α_p, 10^{-4} K^{-1})

m	p	T						
		348.15	373.15	398.15	423.15	473.15	523.15	573.15
0.097	50	5.96	7.20	8.44	9.73	13.00	18.70	–
	200	5.81	6.99	8.14	9.31	12.07	16.43	24.23
	400	5.58	6.74	7.87	8.96	11.25	14.19	18.75
0.2905	50	5.81	6.98	8.14	9.34	12.32	17.39	–
	200	5.67	6.77	7.85	8.94	11.47	15.39	22.35
	400	5.52	6.55	7.55	8.54	10.65	13.48	18.07
0.571	50	5.65	6.71	7.76	8.84	11.46	15.78	–
	200	5.53	6.53	7.50	8.49	10.73	14.12	20.09
	400	5.43	6.32	7.19	8.06	9.95	12.58	16.99
0.895	50	5.57	6.51	7.45	8.40	10.70	14.46	–
	200	5.45	6.35	7.23	8.12	10.13	13.12	18.39
	400	5.33	6.15	6.94	7.73	9.44	11.78	15.64

mass of the solution in the piezometer. The error of determination of the density in relation to the temperature was 0.03%; it was 0.001% in relation to the pressure and 0.001% in relation to the concentration. The total relative error in determining the density of the solutions did not exceed 0.06%.

The obtained experimental values of the density of the $BaCl_2$ aqueous solutions are presented in Table 1.

A comparison of the experimental data and the literature data [7–10] has shown their good convergence at low (to 75^{o}C) temperatures; the maximum discrepancies attain 0.09%. In the range of temperatures 100–140^{o}C, the discrepancies with [10] do not exceed 0.14%. As has already been noted, we found no data for higher temperatures in the literature.

Our work also sought to obtain the equation of state since it contains extensive information on various properties of a substance in compact form. Using this equation, one can compute the values of all excess calorific functions, thermal coefficients, and the thermodynamic velocity of sound versus the parameters of state and other thermodynamic quantities. In [13], it has been established that in the range 298–573 K the expression most accurately describing the temperature dependence of the specific volumes of water and hence the aqueous solutions of electrolytes has the form

$$v_s = A + Bt + Ct^2 + Dt^7 . \tag{1}$$

TABLE 4. Coefficients of Isothermal Compressibility at Different Temperatures and a Prescribed Concentration (β_T, 10^{-5} bar^{-1})

m	p	T						
		348.15	373.15	398.15	423.15	473.15	523.15	573.15
0.097	50	4.41	4.71	5.18	5.85	8.26	13.87	–
	200	4.32	4.62	5.00	5.51	7.28	11.67	22.39
	400	4.20	4.50	4.77	5.03	5.92	8.56	16.11
0.2905	50	4.28	4.57	5.01	5.63	7.81	12.80	–
	200	4.09	4.35	4.72	5.23	6.97	10.92	20.03
	400	3.83	4.04	4.32	4.68	5.81	8.25	13.86

TABLE 5. Partial Molar Volumes of the Electrolyte $\overline{V}_2$

m	p	T						
		298.15	323.15	373.15	423.15	473.15	523.15	573.15
0.097	100	33.3	33.0	29.6	22.1	8.0	–21.4	–88.8
	200	33.6	33.7	30.7	23.4	10.0	–15.7	–69.6
	400	32.8	35.3	34.8	27.0	12.3	–8.6	–33.2
0.2905	50	31.8	31.8	29.2	22.5	9.8	–16.5	–75.5
	200	32.2	32.5	30.2	23.8	11.9	–10.8	–58.0
	400	32.0	34.0	33.3	26.7	14.2	–4.2	–27.9
0.571	50	31.9	32.6	31.4	26.4	16.2	–4.1	–47.7
	200	32.6	33.3	32.2	27.6	18.5	1.3	–33.4
	400	33.4	34.4	33.8	29.3	20.7	7.0	–14.5
0.895	50	35.6	37.2	38.0	35.6	29.4	17.9	–3.1
	200	36.6	37.8	38.5	36.6	31.8	22.8	6.3
	400	38.6	38.5	37.9	36.6	33.9	27.1	9.5

For the solution of electrolytes, A, B, C, and D are functions of the pressure and the concentration:

$$A = \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij} p^i m^j , \tag{2}$$

where a_{ij} are the empirical coefficients. The analogous formulas have been taken for the coefficients B, C, and D. The values of the empirical coefficients a_{ij}, b_{ij}, c_{ij}, and d_{ij} are given in Table 2.

In some cases, it is convenient to use an equation describing the dependence of the relative specific volume (relative density) on the parameters of state. Such an equation must not contain a large number of empirical coefficients as a rule. In this work, an equation of compact form containing only four empirical coefficients and describing the dependence of the relative specific volume on the parameters of state is proposed in the form

$$\frac{v_s}{v_w} = (a_1 + a_2 m) + (b_1 + b_2 m)\, t^6 , \tag{3}$$

where $a_1 = 0.99328$, $a_2 = -0.13925$, $b_1 = -1.352567 \cdot 10^{-4}$, and $b_2 = -6.310696 \cdot 10^{-4}$.

Using Eq. (1), we calculated the basic volume characteristics of the solutions: the coefficients of thermal expansion α_p (Table 3) and isothermal compressibility β_T (Table 4) and the partial molar volumes of the electrolyte $\overline{V}_2$ (Table 5).

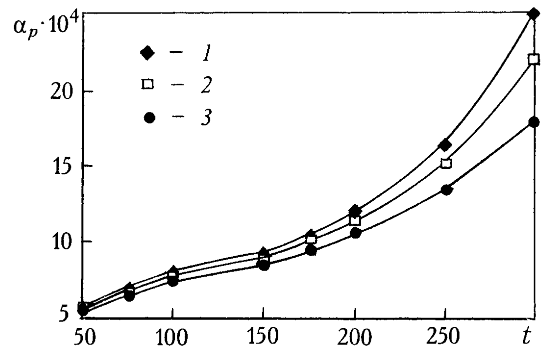

Fig. 1. Temperature dependence of the coefficients of thermal expansion α_p for solutions with a concentration of 0.29 mole/kg H_2O: 1) 10, 2) 20, and 3) 40 MPa. α_p, K^{-1}; t, ^oC.

The quantity α_p increases with increase in the temperature (see Fig. 1) and decreases with increase in the pressure. The dependence of the compressibility β_T on the parameters of state is qualitatively similar to the dependence of α_p. The coefficient of thermal expansion [14] can be considered as the sum of the vibrational and configurational contributions: $\alpha_p = \alpha_{vibr} + \alpha_{conf}$. As the temperature increases, the tetrahedral structure of water becomes weaker and gradually fails, because of which the volume of the liquid decreases. This effect corresponds to the configurational contribution and has a negative sign. At the same time, the amplitudes of anharmonic intermolecular vibrations increase in heating, which causes the liquid to expand. The latter effect corresponds to the vibrational contribution to the quantity α_p and has a positive sign. Experimental data demonstrate that α_p continuously increases with temperature at fixed pressure and concentration; by this is meant that the vibrational contribution α_{vibr} prevails over the configurational contribution α_{conf} in the entire temperature range in question and that the former is increasing in primary importance with increase in the temperature.

The partial molar volumes $\overline{V}_2$ of the electrolyte were calculated from the formula

$$\overline{V}_2 = M_2 v_s + (1000 + mM_2)\,\frac{\partial v_s}{\partial m}\,,$$

and the data obtained are given in Table 5. The increase in pressure in the system leads to an increase in $\overline{V}_2$. The temperature dependence of the $\overline{V}_2$ of the electrolyte is extremum in character with a maximum at 320–370 K; as the salt content increases, the extremum shifts in the direction of higher temperatures. Addition of new portions of the electrolyte to the solution leads to an increase in $\overline{V}_2$.

CONCLUSIONS

1. The proposed analytical dependence of the relative specific volume on the temperature (3) enables one to describe experimental data in a wide temperature range (298–573 K), using as few empirical coefficients as possible.

2. It has been established that the dependence of the partial molar volume of the electrolyte in the system $BaCl_2$–H_2O is extremum in character with a maximum in the range 320–370 K.

NOTATION

V, volume of the piezometer, cm^3; v_s, specific volume, 10^{-3} m^3/kg; t, temperature, ^oC; $T = t + 273.15$, temperature, K; P, pressure, 10^5 Pa; m, molarity, mole/kg H_2O; α_p, coefficient of thermal expansion K^{-1}; β_T, coefficient of isothermal compressibility, bar^{-1}; $\overline{V}_2$, partial molar volume of the electrolyte, 10^{-6} m^3/mole; M_2, molecular mass of the salt, g/mole; ρ, density, g/cm^3. Subscripts: s, solution; w, water; vibr, vibrational; conf, configurational; 2, second component.

REFERENCES

1. N. D. Azizov, T. S. Akhundov, and V. I. Zarembo, *Zh. Prikl. Khim.*, **65**, No. 2, 440–443 (1992).
2. N. D. Azizov, T. S. Akhundov, and V. I. Zarembo, in: *Geothermy. Geological and Thermophysical Problems* [in Russian], Makhachkala (1992), pp. 195–196.
3. N. D. Azizov, *Teplofiz. Vys. Temp.*, No. 3, 379–385 (1997).
4. N. D. Azizov and T. S. Akhundov, *Zh. Fiz. Khim.*, **71**, No. 11, 1959–1962 (1997).
5. N. D. Azizov, *Russ. J. Gen. Chem.*, **67**, No. 4, 527–531 (1997).
6. N. D. Azizov and T. S. Akhundov, *Zh. Neorg. Khim.*, No. 10, 1723–1727 (1998).
7. V. I. Perel'man (ed.), *Chemist's Handbook* [in Russian], Vol. 3, Moscow–Leningrad (1964).
8. *International Critical Tables*, Vol. 3, New York (1928), p. 78.
9. A. N. Baranov and B. R. Churagulov, in: *Physical and Physicochemical Properties of Substances at High Parameters. Hydrothermal Systems* [in Russian], Moscow (1988), pp. 8–11.
10. D. Puchalska and G. Atkinson, *J. Chem. Eng. Data*, **36**, No. 4, 449–452 (1991).
11. N. D. Azizov, *Zh. Neorg. Khim.*, No. 2, 323–326 (1998).
12. N. D. Azizov, *Thermophysical Properties of Water–Salt Systems* [in Russian], Baku (1999).
13. N. D. Azizov, T. S. Akhundov, and L. A. Azizova, *Teplofiz. Vys. Temp.*, No. 6, 973–977 (1996).
14. D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* [Russian translation], Leningrad (1975).