

Table II. Analysis of the Available ΔH_s Data for the RbBr Using the Two Methods Explained in the Text

method	ref	$\Delta H_s^\infty /$ (J mol ⁻¹)	$B /$ (J kg mol ⁻²)	$s /$ (J mol ⁻¹)
L_ϕ data	4	22185 ± 34		
	this work	22207 ± 61		
eq 3	4	22182 ± 72	-3384 ± 1197	39
	this work	22166 ± 35	-2394 ± 994	65

of $L_\phi(m)$, the relative apparent molar enthalpy, is necessary. The only available experimental values of $L_\phi(m)$ for RbBr aqueous solutions at 298.15 K are from Fortier et al. (9). On the other hand, the experimental values of ΔH_s could be analyzed in terms of an equation in m and the value at infinite dilution found as the intercept at zero molality. In a previous work (10) it was shown that the following expression can be used satisfactorily (for 1-1 electrolytes) in the molality range covered in this work

$$\Delta H_s = \Delta H_s^\infty + A_H m^{1/2} \left\{ \frac{1}{(1+m^{1/2})} - [\sigma(m)/3] \right\} + Bm \quad (3)$$

where

$$\sigma(m) = \left(3/m^{1/2} \right) \left\{ 1 + m^{1/2} - [1/(1+m^{1/2})] - 2 \ln(1+m^{1/2}) \right\}$$

A_H is the Debye-Hückel limiting slope (11), ΔH_s^∞ and B are adjustable parameters.

In the first possibility the enthalpy of solution at infinite dilution, ΔH_s^∞ , is obtained as the mean of the extrapolated values. The uncertainty is the standard deviation of the mean. By use of eq 3 the values of ΔH_s^∞ and B are obtained by the least-squares method. The uncertainty in the estimation of the adjustable parameters P (B and ΔH_s^∞) has been calculated as (12)

$$\sigma^2(P) = s^2 \sum_i \left(\frac{\partial P}{\partial y_i} \right)^2 \quad (4)$$

where y_i represent the experimental values of ΔH_s and s the standard deviation of the fit

$$s = \left[\frac{\sum_i (\Delta H_{s(\text{calc})} - \Delta H_{s(\text{exp})})^2}{n - q} \right]^{1/2} \quad (5)$$

In eq 5, n is the number of experimental data and q is the number of parameters.

The experimental data presented in Table I and those reported by Weintraub et al. (4) have been analyzed by using the two methods explained above. The results are summarised in

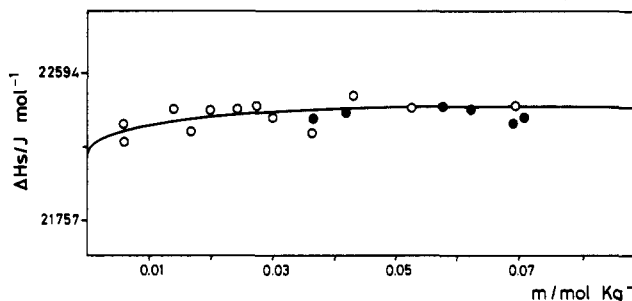


Figure 1. Plot of ΔH_s against molality. Reference 4 (●); present work (○); fit of the experimental values presented in this work by means of eq 3 (—).

Table II. One can see that no appraisable differences exist, within the error, between the two data sets and the two extrapolation methods employed. The agreement is not only restricted to ΔH_s^∞ values. The molality dependence of ΔH_s , reflected on the parameter B , is the same in the common molality range. This behavior can be seen clearly in Figure 1. For this reason, we think that a reliable value of ΔH_s^∞ could be obtained using our ΔH_s data combined with those of Weintraub et al. (4). The proposed value of ΔH_s^∞ for RbBr in water at 298.15 K is

$$\Delta H_s^\infty(298.15 \text{ K}) = (22179 \pm 28) \text{ J mol}^{-1}$$

The value has been obtained after extrapolating the combined data by means of eq 3.

Registry No. RbBr, 7789-39-1.

Literature Cited

- (1) Parker, V. B. "Thermal Properties of Aqueous Uni-univalent Electrolytes"; *Natl. Bur. Stand. (U.S.)* 1965; p 31-32.
- (2) Lange, E.; Martin, W. Z. *Phys. Chem.* 1937, **A180**, 233-245.
- (3) Thourey, J.; Perachon, G. *Thermochim. Acta* 1980, **39**, 243-252.
- (4) Weintraub, R.; Apelblat, A.; Tamir, A. *J. Chem. Thermodyn.* 1982, **14**, 887-892.
- (5) Sanahuja, A.; Cesari, E. *J. Chem. Thermodyn.* 1984, **16**, 1195-1202.
- (6) Landolt-Börnstein. *Kalorische Zustandsgrößen*; Springer Verlag: West Berlin, 1961; II Band, 4 Teil; p 487.
- (7) Desnoyers, J. E.; de Visser, C.; Perron, G.; Picker, P. *J. Solution Chem.* 1976, **5**, 605-616.
- (8) McGlashan, M. L. *Chemical Thermodynamics*; Academic: London, 1979; p 68-69.
- (9) Fortier, J. L.; Leduc, P. A.; Desnoyers, J. E. *J. Solution Chem.* 1974, **3**, 323-349.
- (10) Sanahuja, A.; Gómez-Estévez, J. L. *Thermochim. Acta* 1985, **94**, 223-229.
- (11) Clarke, E. C. W.; Glew, D. N. *J. Chem. Soc., Faraday Trans. 1* 1980, **76**, 1911-1916.
- (12) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; p 113.

Received for review September 23, 1985. Accepted February 5, 1986.

Densities of Aqueous Strontium Chloride Solutions up to 200 °C and at 20 bar

Anil Kumar

Institute of Physical Chemistry and Electrochemistry, University of Karlsruhe, D 7500 Karlsruhe, West Germany

Densities of aqueous SrCl_2 are reported from 50 to 200 °C at 20.27 bar pressure up to a concentration of 2.7 mol kg^{-1} . Apparent molal volumes calculated from densities can be fitted with Pitzer's equations with a standard deviation of 0.09 $\text{cm}^3 \text{mol}^{-1}$.

Introduction

Aqueous solutions of alkali and alkaline earth metal chlorides are important components of natural brines and are used in industrial processes. A literature survey reveals that density data on these solutions especially at high temperatures and

Table I. Densities of Aqueous Strontium Chloride at 20.27 bar and Various Temperatures

m , mol kg ⁻¹	d , g cm ⁻³						
	50	75	100	125	150	175	200
0	0.98801	0.97572	0.95930	0.93999	0.91794	0.89308	0.86510
0.3029	1.02959	1.01614	0.99974	0.98093	0.95947	0.93546	0.90907
0.5182	1.05780	1.04419	1.02775	1.00907	0.98803	0.96450	0.93855
0.7914	1.09262	1.07862	1.06235	1.04375	1.02294	1.00005	0.97486
1.0406	1.12379	1.10956	1.09323	1.07477	1.05429	1.03159	1.00706
1.3743	1.16410	1.14979	1.13347	1.11565	1.09559	1.07345	1.04908
1.6628	1.19810	1.18342	1.16764	1.14987	1.13062	1.10877	1.08456
2.1281	1.25108	1.23669	1.22070	1.20351	1.18588	1.16456	1.14012
2.7175	1.31526	1.30048	1.28527	1.27001	1.25400	1.23938	1.20888

concentrations are lacking. Densities are very useful in estimating the pressure dependence of activity coefficients. Ellis (1, 2) published precise density data for these solutions up to 200 °C but only to a concentration of 1 m . Rogers et al. (3) have recently measured the densities of aqueous NaCl up to 200 °C and 20.27 bar pressure. In this paper, we present experimental densities of aqueous SrCl₂ solutions from 50 to 200 °C at 20.27 bar and up to a concentration of 2.7 mol kg⁻¹. Apparent molal volumes calculated from these densities are treated with Pitzer's equations (4) for single aqueous electrolytes.

Experimental Section

SrCl₂ from BDH (AR grade) was recrystallized from water and dried before use. Solutions were made by dissolving a definite mass in deionized water. The concentration of stock solution was determined gravimetrically as AgCl.

Densities were measured with a dilatometer similar to that of Rogers et al. (3). The volume of the pressure cell was about 11 cm³. The pressure cell was kept in an oil bath accurate to ±0.05 °C up to 125 °C and ±0.1 °C from 150 to 200 °C. The reference vessel was set at 25 ± 0.01 °C. The densities of the SrCl₂ solutions at the reference temperature of 25 °C were taken from elsewhere (5). Accurately known densities of SrCl₂ solutions as a function of temperature, pressure, and concentration were obtained from elsewhere (6). The temperature of the oil bath was raised in increments of 25 °C. The entire system was pressurized with a high-pressure nitrogen cylinder. Details of the apparatus and the methods of calibration and experimentation are discussed elsewhere (3). Measured densities were precise to ±2.2 × 10⁻⁴ g cm⁻³ up to 125 °C and ±5.1 × 10⁻⁴ g cm⁻³ to 200 °C.

Results and Discussion

Experimental densities, d , of aqueous SrCl₂ at 20.27 bar pressure and from 50 to 200 °C are given in Table I.

Experimental densities can be easily fitted with a polynomial of the form

$$d - d_0 = Am^{1/2} + Bm + Cm^{3/2} + Dm^2 \quad (1)$$

where m is the molality of the solution and A , B , C , and D are temperature-dependent parameters of the form

$$A = a_0 + a_1T + a_2T^2 + \dots \quad (2)$$

where T is in kelvin and d_0 is the density of pure water, taken from elsewhere (7). Table II lists these parameters along with the standard deviation of fit.

Apparent molal volumes ϕ_v obtained from these densities are plotted in Figure 1 as a function of $m^{1/2}$. As is apparent from this figure, our measurements in the lower concentrations are in good agreement with those of Ellis (2).

Table II. Temperature-Dependent Parameters of Eq 1 for Calculating the Density^a of Aqueous SrCl₂ Solutions

parameters	values	parameters	values
a_0	-0.3195	C_0	-2.0340
a_1	0.2454×10^{-2}	C_1	0.0173
a_2	-0.6073×10^{-5}	C_2	-0.4502×10^{-4}
a_3	0.4864×10^{-8}	C_3	0.3814×10^{-7}
b_0	1.6871	d_0	0.9530
b_1	-0.0132	d_1	-0.7585×10^{-2}
b_2	0.3334×10^{-4}	d_2	0.1907×10^{-4}
b_3	-0.2748×10^{-7}	d_3	-0.1455×10^{-7}

^aStandard deviation in density = 3.1×10^{-4} g cm⁻³.

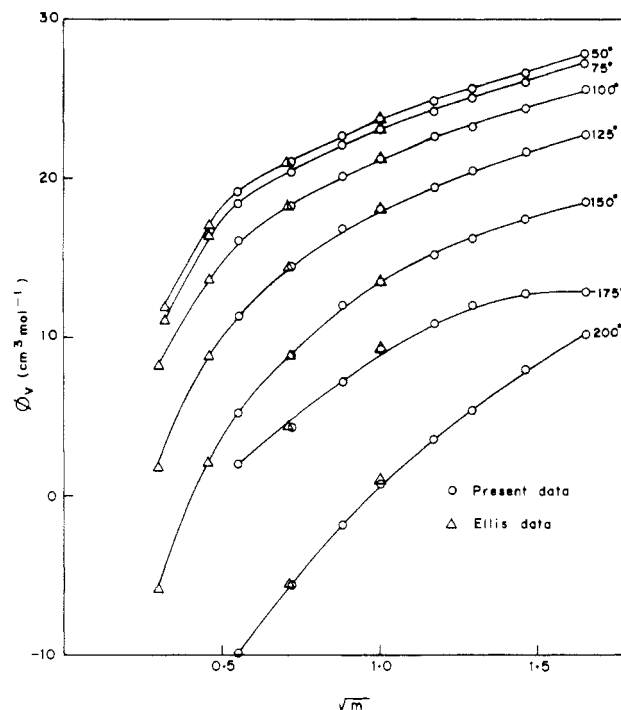


Figure 1. ϕ_v vs. $m^{1/2}$ for aqueous SrCl₂ solutions up to 200 °C and at 20 bar pressure.

ϕ_v of these solutions can be analyzed by using Pitzer's equation (4). Pitzer's equations for a 2-1 salt like SrCl₂ can be simplified to read

$$\phi_v = \phi_v^0 + 3(A_v/b) \ln(1 + bI^{1/2}) + 4RT[mB^V + 2m^2C^V] \quad (3)$$

where

$$B^V = \left(\frac{\partial \beta^{(0)}}{\partial p} \right)_T + \left(\frac{\partial \beta^{(1)}}{\partial p} \right)_T \frac{2}{\alpha^2 I} [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (4)$$

$$C^V = \left(\frac{\partial c^\phi}{\partial p} \right)_T / 2.8284 \quad (5)$$

Table III. Temperature Dependence of Pitzer Coefficients for Aqueous SrCl₂ at 20.27 bar and from 50 to 200 °C Using Eq 6

Pitzer coeff	10 ² q ₀	10 ⁴ q ₁	10 ⁶ q ₂	10 ⁸ q ₃	10 ⁶ σ
(∂β ⁰ /∂P) _T	0.8056	-0.6303	0.1645	-0.1425	0.81
(∂C ^φ /∂P) _T	0.2607	-0.2027	0.0508		0.05

ϕ_V^0 is the partial molal volume at infinite dilution. A_V , the Pitzer-Debye-Hückel slope was either calculated or taken from the method and compilations of Bradley and Pitzer (8), Rogers and Pitzer (4) and Ananthaswamy and Atkinson (9). α and b are 2.0 and 1.2 (kg/mol)^{1/28} respectively, while R is 83.1441 cm³ bar mol⁻¹ K⁻¹.

A nonlinear least-squares program was employed for generating Pitzer's coefficients by using eq 3, 4, and 5. Rogers and Pitzer (4) reported that the $(\partial\beta^{(1)}/\partial P)_T$ term is insignificant at higher molalities and found it difficult to evaluate it for aqueous NaCl solutions. We too find this term to be negligible in aqueous SrCl₂. The lower concentration data of Ellis (2) were also included in the overall fit. ϕ_V^0 values obtained by Ellis (2) were used in eq 3. $(\partial\beta^{(0)}/\partial P)_T$ and $(\partial C^\phi/\partial P)_T$ thus obtained were fitted with the polynomial of the form

$$Y = q_0 + q_1 T + q_2 T^2 + q_3 T^3 \quad (6)$$

Temperature-dependent parameters q_0 , q_1 , q_2 , and q_3 for both Pitzer's parameters are given in Table III. The average standard deviation of the fit for ϕ_V , using Pitzer's equations, is 0.09 cm³ mol⁻¹ from 50 to 200 °C and at 20.27 bar pressure.

Acknowledgment

The late C. V. G. Reddy of Goa helped me in the experimentation and with stimulating discussions.

Registry No. SrCl₂, 10476-85-4.

Literature Cited

- (1) Ellis, A. J. *J. Chem. Soc. A* 1966, 1579.
- (2) Ellis, A. J. *J. Chem. Soc. A* 1966, 606.
- (3) Rogers, P. S. Z.; Bradley, D. J.; Pitzer, K. S. *J. Chem. Eng. Data* 1982, 27, 47.
- (4) Rogers, P. S. Z.; Pitzer, K. S. *J. Phys. Chem. Ref. Data* 1982, 11, 15.
- (5) Isono, T. *J. Chem. Eng. Data* 1984, 29, 45.
- (6) *International Critical Tables*; McGraw-Hill: New York, 1928; Vol. 3.
- (7) Grigull, U. *Properties of Water and Steam*, 3rd ed.; Springer: Heidelberg, West Germany, 1982.
- (8) Bradley, D. J.; Pitzer, K. S. *J. Phys. Chem.* 1979, 83, 1599.
- (9) Ananthaswamy, J.; Atkinson, G. *J. Chem. Eng. Data* 1984, 29, 81.

Received for review September 30, 1985. Accepted January 13, 1986.

Vapor-Liquid Equilibria for Model Mixtures of Coal-Derived Liquids. 1. Binary Systems with 2-Methylfuran

David H. Krevor[†] and John M. Prausnitz*

Chemical Engineering Department, University of California, Berkeley, California 94720

Vapor-liquid equilibria were measured for binary systems of 2-methylfuran with cyclohexane, benzene, thiophene, and pyridine in the region 45–65 °C. Deviations from ideal behavior are small, especially for 2-methylfuran/aromatic binaries. In binary solutions with benzene or cyclohexane, 2-methylfuran shows smaller deviations from ideality than those observed for other aromatic heterocycles (pyridine and thiophene). For nearly ideal mixtures, complex models for the excess Gibbs energy (such as UNIQUAC) may give spurious results. For nearly ideal systems, it is advantageous to use a simple model.

Introduction

Interest in coal liquefaction and gasification tends to be inversely proportional to the availability of petroleum. At various times in this century, there has been significant interest in the use of coal to produce liquid fuels and feedstocks for petrochemicals (1). Such interest has been sporadic, always coinciding with periods of high relative petroleum cost.

To design efficient separation operations, it is necessary to appreciate the differences between petroleum-derived and coal-derived liquids. For engineering design, a primary concern is to understand vapor-liquid equilibria of coal-derived liquids.

The chemical composition of coal (2) differs significantly from that of oil. A major distinction is the heteroatom content. The sulfur, nitrogen, and oxygen content of coal (3) is typically an

order of magnitude above that in oil (independent of whatever inorganic material may be present in the coal). To predict phase equilibria for mixtures containing coal-liquefaction products, it is necessary to know the influence of the heteroatom groups on fluid-phase thermodynamic properties.

The oxygen content of bituminous coal is usually about 15 wt % on a moisture and ash-free basis (1). The predominant functional groups include phenols, ethers, carboxylic acids, carbonyls, and furans. We are particularly interested in furans because deoxygenation of heterocyclic oxygen is more difficult than that for oxygen outside of a ring structure (4).

There is a paucity of vapor-liquid equilibrium data for mixtures containing aromatic, oxygen heterocycles. We are not aware of any vapor-liquid equilibrium data in the literature for mixtures of furan or a substituted furan with benzene (or any other aromatic) or with any alkane other than butane (5). Such data are necessary to provide a data base for estimation methods such as UNIFAC (6) or ASOG (7).

In part 1 of this work, we report vapor-liquid equilibria for binary mixtures of 2-methylfuran with benzene, cyclohexane, thiophene, and pyridine. Part 2 presents results for binary mixtures containing bicyclic and high-boiling compounds (diphenyl ether, tetralin, *m*-cresol, 1-methylnaphthalene, quinoline, aniline, and benzothiazole). Part 3 reports vapor-liquid equilibrium data for ternary systems containing one aromatic heterocycle (2-methylfuran, thiophene, pyridine, or pyrrole) with benzene and cyclohexane.

Experimental Section

All chemicals are commercially available. Benzene, cyclohexane, pyridine, and thiophene were spectrophotometric or high-purity grade; they were not purified further. The 2-

[†] Present address: Raychem Corporation, 300 Constitution Drive, Menlo Park, CA 94025.