Registry No. Cyclohexene, 110-83-8; cyclohexane, 110-82-7; 1,2-dichloroethane, 107-06-2.

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Molality Dependence of the Differential Enthalpies of Solution of RbBr in Water at 298.15 K

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The differential enthalpies of solution of RbBr in water at 298.15 K were measured in the molality range 0.1–5.0 mol kg^{-1}. The experimental system was a Tian-Calvet calorimeter type adapted to this particular case and tested in previous works. From the experimental results the molality dependence of the relative apparent molar enthalpy $L_\phi(m)$ has been obtained up to 5.0 mol kg^{-1}.

Introduction

There is in general a lack of information about the enthalpies of the aqueous solutions of rubidium halides and RbBr in particular (1–3). In a previous work (*4*), the enthalpies of solution of RbBr in water at 298.15 K and at low molalities (<0.071 mol kg^{-1}) were measured. From the measurements and the literature data the enthalpy of solution at infinite dilution was obtained (*4*).

With respect to the molality dependence of the enthalpy of the aqueous solutions of RbBr, the situation is worse. The only experimental study until now has been made by Fortier et al. (*5*). They measured the enthalpies of dilution in the molality range 0.04–0.96 mol kg^{-1} by using a Picker microcalorimeter, and the molality dependence of the relative apparent molar enthalpy $L_\phi(m)$ was obtained.

The purpose of this work was to extend our knowledge of the L_ϕ's to higher molalities. The method employed was based on the experimental determination of the differential enthalpies of solution $\Delta_{sol}H_2$ of RbBr in water at 298.15 K. The molality range covered was from 0.1 to 5.0 mol kg^{-1}. The obtention of L_ϕ from $\Delta_{sol}H_2$ was developed and tested in two previous works (*6*, *7*) for NaCl and KCl aqueous solutions in water at 298.15 K in the whole molality range.

Experimental Section

The differential enthalpies of solution were measured with a Tian-Calvet calorimeter type described in detail in previous works (*6*, *8*). The experimental procedure was described previously (*6*).

For each measurement of the differential enthalpy of solution the temperature was determined within ±0.02 K, an electrical calibration was carried out before and after each solution process, and the initial mechanical effect was corrected as explained earlier (*6*). The calorimetric resolution is 0.02 J and the reproducibility of the measurements is better than 1%.

Table I. Calorimetric Differential Enthalpies of Solution of RbBr in Water at 298.15 K

m, mol kg^{-1}	Δm, mol kg^{-1}	T, K	$\Delta_{sol}H_2^{expt1}(T)$, J mol^{-1}	$\Delta_{sol}H_2^{expt1}$(298.15 K), J mol^{-1}	ϵ, J mol^{-1}
0.100 33	0.013 80	298.30	22 196	22 223	27
0.116 54	0.023 54	298.12	22 401	22 396	13
0.202 99	0.019 43	298.12	22 221	22 216	92
0.306 96	0.021 06	298.12	22 054	22 049	35
0.502 66	0.020 40	298.25	21 384	21 400	17
0.700 98	0.017 07	298.25	21 179	21 195	40
0.705 59	0.019 82	298.47	21 150	21 167	24
0.844 12	0.015 56	298.47	21 094	21 143	78
1.001 97	0.020 52	298.19	20 656	20 662	40
1.201 44	0.016 94	298.07	20 251	20 238	49
1.500 58	0.018 43	298.22	19 728	19 737	35
1.701 43	0.020 40	298.25	19 652	19 667	68
2.002 04	0.020 72	298.25	19 020	19 033	18
2.009 83	0.017 29	298.24	19 046	19 057	85
2.502 32	0.019 99	298.31	18 351	18 370	69
3.002 16	0.020 17	298.25	17 531	17 542	37
3.502 12	0.018 20	297.95	17 029	17 009	50
4.001 55	0.018 21	298.07	16 406	16 398	23
4.501 78	0.018 53	298.07	15 803	15 797	36
5.001 76	0.015 82	298.07	15 472	15 467	47

The water used was doubly distilled, and the solid sample was Merck Suprapur. It was heated for 5 h in a furnace at 774 ± 5 K. The molalities are better than 0.01%, and the solute weighings are accurate to 0.003%.

Experimental Results

The measured differential enthalpies of solution of RbBr in water at 298.15 K are shown in Table I. The results were obtained by adding a small amount Δn_2 of solid salt to a solution of original molality m. Δm is the change of molality after the solution process, $\Delta_{sol}H_2^{expt1}(T)$ is the experimental differential enthalpy of solution at T, and $\Delta_{sol}H_2^{expt1}$(298.15 K) is the experimental differential enthalpy of solution adjusted to 298.15 K and after correcting for the error due to condensation of solvent vapor over the solution.

In Table I, ϵ is the estimated error in each calorimetric measurement. The values of ϵ were calculated from the uncertainties in the total energy change due to the noise in the base-line calorimeter.

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Table II. Results of the Weighted Least-Squares Fit of $\Delta_{sol}H_2$(RbBr,aq) at 298.15 K by Means of Eq 10

A_2, J kg mol^{-2}	A_3, J kg$^{3/2}$ mol$^{-5/2}$	A_4, J kg^2 mol^{-3}	A_5, J kg$^{3/2}$ mol$^{-7/2}$
−4678 ± 66	2986 ± 113	−1057 ± 64	150 ± 12

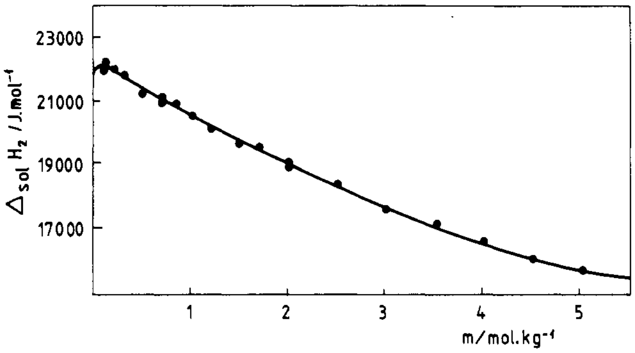

Figure 1. Plot of $\Delta_{sol}H_2$ against molality. Experimental values from Table II (●); fit of the experimental data by means of eq 10 (—).

The adjustments to 298.15 K were computed by using the expression (*6*)

$$\Delta_{sol}H_2(298.15\ \mathrm{K}) = \Delta_{sol}H_2(T) + [(\partial\Delta_{sol}H_m^\infty/\partial T) + (C_{p,2} - C_{p,2}^\infty)](298.15\ \mathrm{K} - T) \quad (1)$$

where $\Delta_{sol}H_m^\infty$ is the enthalpy of solution at infinite dilution and $C_{p,2} - C_{p,2}^\infty$ is given by

$$C_{p,2} - C_{p,2}^\infty = (\partial L_2/\partial T)_{p,m} = (\partial[m(C_{p,\phi} - C_{p,\phi}^\infty)]/\partial m)_{T,p} \quad (2)$$

where L_2 is the relative partial molar enthalpy and $C_{p,\phi}$ and $C_{p,\phi}^\infty$ are the apparent molar heat capacities of the dissolved salt at molality m and at infinite dilution, respectively. Literature values for $(C_{p,\phi} - C_{p,\phi}^\infty)$ (*3*, *9*, *10*) and $(\partial\Delta_{sol}H_m^\infty/\partial T)$ (*11*) were used.

The error due to condensation of solvent is given by (*6*)

$$\delta\Delta_{sol}H_2 = (p_f - p_i)V_m^g\,\Delta_l^gH_m^*/RT \quad (3)$$

where V_m^g is the molar volume of the vapor phase, p_i and p_f are the vapor pressures of the solvent vapor over the solution before and after the solution process, and $\Delta_l^gH_m^*$ is the molar enthalpy of evaporation of pure solvent. $\Delta p = (p_f - p_i)$ is given by

$$\Delta p = p^*[\exp(-2(m + \Delta m)M_1\phi_f) - \exp(-2mM_1\phi_i)] \quad (4)$$

where p^* is the vapor pressure of the pure solvent, $M_1 = 18.0153 \times 10^{-3}$ kg mol^{-1} is the molar mass of pure solvent, and ϕ_i and ϕ_f are the osmotic coefficients before and after the solution process. Literature values of ϕ for RbBr solutions were used (*12*).

Discussion

The differential enthalpy of solution $\Delta_{sol}H_2$ is defined as (*6*)

$$\Delta_{sol}H_2 = (\partial\Delta_{sol}H/\partial n_2)_{T,p,n_1} = \Delta_{sol}H_m^\infty + L_2(m) \quad (5)$$

where $\Delta_{sol}H$ is the enthalpy of solution and n_1 and n_2 are the amounts of substance of solvent and solute, respectively.

In a real solution process where a small amount Δn_2 of solid salt is added to a solution of original molality m, the enthalpy change ΔH is given by

$$\Delta H = \int_{n_2}^{n_2+\Delta n_2} \Delta_{sol}H_2\,dn_2 \quad (6)$$

and using 5, the experimental differential enthalpy of solution $\Delta_{sol}H_2^{expti}$ can be written as

$$\Delta_{sol}H_2^{exptl} = \Delta H/\Delta n_2 = \Delta_{sol}H_m^\infty + (1/\Delta m)\int_m^{m+\Delta m} L_2(m)\,dm \quad (7)$$

By using a thermodynamic relation between L_2 and L_ϕ

$$L_\phi(m) = (1/m)\int_0^m L_2(m)\,dm \quad (8)$$

and assuming a molality dependence for $L_\phi(m)$

$$L_\phi(m) = \sum_{j=1}^{n} A_j m^{j/2} \quad (9)$$

eq 7 can be written as

$$\Delta_{sol}H_2^{exptl} = \Delta_{sol}H_m^\infty + \sum_{j=1}^{n} A_j((m + \Delta m)^{3j/2} - m^{3j/2})/\Delta m \quad (10)$$

In eq 9, the A_j's ($j \le n$) are adjustable parameters with the exception of $j = 1$. A_1 corresponds to the Debye–Hückel limiting slope for L_ϕ.

The experimental differential enthalpies of solution summarized in Table I were fitted to eq 10 by using a weighted least-squares method. Literature values for $\Delta_{sol}H_m$ (*4*) and the limiting slope for L_ϕ and A_1 (*13*) were used. The minimum number of adjustable parameters ($n - 1$) was determined from the standard deviations in the usual manner (*14*). The standard deviation of the fit s (*4*) was found to be 111 J mol^{-1} with four adjustable parameters. The results of the weighted least-squares fit of $\Delta_{sol}H_2$ by means of eq 10 are summarized in Table II. The uncertainty in the estimations of the adjustable parameters A_j (j = 2–n) has been calculated as (*15*)

$$\sigma^2(A_j) = \sum_{i=1}^{n}(\partial A_j/\partial R_i)^2\epsilon_i^2 \quad (11)$$

where

$$R_i = \Delta_{sol}H_2^{exptl}(i) - \Delta_{sol}H_m^\infty - A_1[(m + \Delta m)_i^{3/2} - m_i^{3/2}]/\Delta m_i \quad (12)$$

for each experimental measurement i, and n is the number of experimental data. In Figure 1, the experimental results are plotted against m jointly with the fitted expression for $\Delta_{sol}H_2$. With the fitted values of A_j ($2 \le j \le 4$) the molality dependence of L_ϕ for RbBr at 298.15 K can be computed by means of eq 9 up to 5.0 mol kg^{-1}.

Following Fortier et al. (*5*), our results had been tested by comparing their experimental enthalpies of dilution with the $\Delta L_\phi = L_\phi(m_f) - L_\phi(m_i)$ calculated from eq 9 between the final and initial molalities. In the common molality range covered by the two works the differences were found to be lower than 16 J mol^{-1}. The agreement is within the experimental uncertainties and comparable with the values obtained for other electrolytes in ref *5*.

Registry No. RbBr, 7789-39-1.

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Solubility of 1-Octadecanol and Stearic Acid in Supercritical Carbon Dioxide

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By use of a continuous flow facility, the solubility of 1-octadecanol [$CH_3(CH_2)_{16}CH_2OH$] and stearic acid [$CH_3(CH_2)_{16}COOH$] in dense supercritical carbon dioxide has been established at 318, 328, and 338 K and pressures ranging from 140 to 467 bar. Maximum solubilities were observed for both systems at 318 K and pressures of 280–300 bar. The results of the 1-octadecanol–carbon dioxide system at 328 and 338 K and those for the stearic acid–carbon dioxide system at 338 K were correlated with the mole fraction of the solute and the reduced density of the pure solvent. This approach yielded deviations of 5.85% (13 points) for 1-octadecanol and 3.39% (5 points) for stearic acid. The Hansen three-dimensional solubility parameter was also applied to the Flory–Huggins theory for the development of a different model which yielded deviations of 24.0% (17 points) for 1-octadecanol and 5.14% (17 points) for stearic acid.

Supercritical extraction presently continues to receive considerable attention as a separation scheme and promises in the near future to be a valuable method for the purification of newly developed specialty chemicals. One of the significant advantages of this method resides in that the solvent can be easily, quickly, and completely separated from the accompanying solute and thus significantly reduce the contamination of valuable compounds with a residual solvent. In this regard, the pharmaceutical and food industries are currently examining the application of supercritical separation processes since there exists the possibility of employing cheap and safe solvents such as carbon dioxide and nitrogen. Background established on supercritical extraction obtained in the past decade now permits the improvement of mechanical design and the performance of continuously operated high-pressure compressors, pressure regulators, and emergency relief systems that make the operation of these processes less troublesome and safer to use. In this regard, it should be noted that a pilot plant for the continuous separation of lecithin from soya oil, as reported by Peters et al. (*1*), is now successfully operational. Based on the results of this pilot plant, current design plans are now in progress for the construction of a commercial plant capable of producing 500 tons/y of raw lecithin. As pointed out by Coenen et al. (*2*) the economics for the re-refining of used lubricating oils employing supercritical extraction is compatible with current methods of recovery.

The substances selected for the present study are 1-octadecanol [$CH_3(CH_2)_{16}CH_2OH$] and stearic acid [$CH_3(CH_2)_{16}COOH$]. Both compounds are extensively used in the pharmaceutical, cosmetic, and surfactant industries where the need for highly purified components is essential. Hardly any fundamental quantitative studies presently exist on the solubility of these two compounds in supercritical gases. The present study was undertaken to establish the possibility of dissolving these compounds in supercritical carbon dioxide at three different temperatures over a wide range of pressures from roughly 140 to 470 bar. The results obtained from this study can prove to be of industrial value for the manufacture and purification of these aliphatic compounds.

Experimental Section

The 1-octadecanol used in this investigation was of reagent grade (CAS no. 112-92-5), was supplied by the Eastman Kodak Co., and was claimed to be of minimum purity of 95% with a claimed melting point range of 329–331 K. The stearic acid, also supplied by the Eastman Kodak Co., was of reagent grade (CAS no. 57-11-4), with a claimed minimum purity of 97% and a melting point range of 341–343 K.

The equipment and procedure used in the present study have been outlined by Kramer and Thodos (*3*). The experimental uncertainties in this study are estimated to be 0.1 K for temperature and ±1.5 bar.

Results

Experimental Measurements. The experimental measurements for the solubility of 1-octadecanol and stearic acid in supercritical carbon dioxide are presented in Tables I and II. These values are also presented in Figures 1 and 2 to show the relationships between y_2, the mole fraction of the solute in the supercritical fluid versus P, the total pressure of the system. To model the supercritical extraction behavior of these systems, two approaches were applied to the data obtained in this study. In the first approach, y_2 was related to the corresponding density of the pure solvent according to the following dependence:

$$\log y_2 = A + B\rho_{R_1} \tag{1}$$

where ρ_{R_1} is the reduced density of the pure solvent. Upon plotting y_2 versus ρ_{R_1} on semilogarithmic coordinates, linear relationships resulted for the 328 and 338 K isotherms of the

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