Solution Behavior of Heavy-Metal Soaps. 1. Solubilities of Mercury(II) Octadecanoate in Water, Formamide, *N*,*N*-Dimethylformamide, and Cyclohexanone at Various Temperatures

Ishwari P. Saraswat and Ramendra Kumar

Chemistry Department, University of Roorkee, Roorkee 247 672, India

Sushil K. Suri*

Chemistry Department, Indian Institute of Technology, New Delhi 110 016, India

The solubilities of mercury(II) octadecanoate (MOD) in water, formamide, *N*,*N*-dimethylformamide, and cyclohexanone have been determined at 5 K intervals over the temperature range 293–328 K by using mercury-203 as a tracer. In water, *N*,*N*-dimethylformamide, and cyclohexanone, the solubility of MOD increases with increase of temperature whereas in formamide it shows a slight decrease. The entropies of solution at 298.15 K calculated from solubility results are indicative of strong solute–solvent interactions resulting in either complexation or intermolecular bonding of MOD with the polar solvents.

Introduction

Heavy-metal soaps are of significant importance as additives in lubricants, emulsifiers in water-in-oil systems, etc. These applications of heavy-metal soaps are a consequence of the difference in their solution properties in aqueous and nonaqueous media (*1–3*). As a part of our investigations on the thermodynamic properties of heavy-metal soap solutions, it became necessary to determine accurately the solubilities of various metal soaps in water and some polar organic solvents wherein these soaps form a clear solution.

In this paper, we report the solubilities of mercury(II) octadecanoate (MOD) in water, formamide, *N*,*N*-dimethylformamide, and cyclohexanone at 5 K intervals over the temperature range 293–328 K. The data reported were obtained by using radioactive mercury-203 as a tracer. The solubilities in water were extrapolated from the solubilities in aqueous sodium perchlorate solutions of varing ionic strength.

Experimental Section

Reagents and Materials. The reagent-grade sample of sodium octadecanoate supplied by BDH was purified by recrystallization from ethanol. All other reagents used were of analytical reagent grade and were used straight from the bottle. The solvents were purified as follows. The water used in the experiments was double glass distilled. Commercial-grade samples of formamide, *N*,*N*-dimethylformamide, and cyclohexanone supplied by BDH were purified according to standard established procedures (*4*). The purified solvents were stored in brown bottles over activated 4A molecular sieves under a dry nitrogen atmosphere and were fractionally distilled immediately before use. The densities and refractive indexes of the solvents agreed closely with the accepted literature values (*4*, *5*).

Preparation of Mercury(II) Octadecanoate. Carrier-free radioisotope mercury-203 obtained in the form of mercury(II) nitrate in dilute nitric acid solution from BARC, India, was added to ~100 mL of aqueous (~0.01 M) mercury(II) chloride solution acidified with hydrochloric acid (pH ~4). The mixture was boiled for 1 h to bring about complete isotopic exchange. The pH of the solution was adjusted to 7 by using sodium hydroxide solution and then an excess of warm solution of sodium octadecanoate (~2%) in ethanol was added gradually with constant stirring to precipitate MOD. The precipitate obtained was washed with warm 50% aqueous ethanol solution until free from chloride ions and excess sodium octadecanoate. It was dried initially under suction and finally in an oven at 110 °C.

The results of the chemical analysis of the sample (C, 56.24%; H, 9.08%; Hg, 26.17%) agreed closely with the stoichiometric ratios (C, 56.33%; H, 9.19%; Hg, 26.13%) in $Hg(C_{18}H_{35}O_2)_2$.

The activity of MOD was determined by dissolving 0.2280 g of the compound in acetone and making up the volume to 250 mL. The number of counts for 5-mL aliquots was determined by using a single-channel γ-ray scintillation spectrometer (BARC, India) provided with a 1-in.-thick crystal of sodium iodide activated with thallium. The following observations were made: average background = 653 counts/5 min; (total counts/5 min)/5-mL aliquot = 32505 (average of five determinations), thus 1 count/min = 9.33×10^{-10} g-ion of Hg^{2+}.

Preparation of Saturated Solutions and Their Analysis. Saturated solutions of MOD in various solvents were prepared by continuous stirring of the two-phase mixture under thermostated conditions for periods of 6–8 h, sometimes starting with unsaturated solvent and other times with solutions which had been saturated at ~5–10 °C higher temperatures. Replicate experiments showed practically no difference in final solute concentration. The technique and the saturator used in the present investigations are similar to those of Glew and Hildebrand (*6*) except that the end of the outlet tube of the saturator dipping in the saturated solution was made of sintered glass. The saturator was thermally insulated by glass wool. The temperature of the circulating water was controlled to ±0.05 °C, and the difference between inlet and outlet temperatures was not greater than 0.08 °C at the highest temperature of determination. After the attainment of saturation, the stirrer was temporarily stopped and the samples of saturated solution were taken for analysis from the bottom stopcock.

The solubilities were determined by taking a known weight (approximately 5 mL) of the saturated solution and estimating the solute in it by counting the radioactive mercury-203 with a single-channel γ-ray spectrometer with the setting and geometry conditions identical with the ones used for determining the specific activity of MOD. Backgrounds for all solutions were measured separately, and an average of three readings of counts/min was used for calculations. Appropriate corrections

0021-9568/84/1729-0200$01.50/0

Table I. Solubilities of Mercury(II) Octadecanoate at Various Temperatures and in Various Solvents

temp, K	solubility, g L^{-1}	$X_{2,\mathrm{satd}}$
	Formamide	
293.15	1.203	6.23×10^{-5}
298.15	1.049	5.45×10^{-5}
303.15	0.936	4.88×10^{-5}
308.15	0.809	4.24×10^{-5}
313.15	0.689	3.62×10^{-5}
318.15	0.634	3.34×10^{-5}
323.15	0.575	3.05×10^{-5}
328.15	0.504	2.68×10^{-5}
	N,*N*-Dimethylformamide	
293.15	0.0198	1.99×10^{-6}
298.15	0.0334	3.37×10^{-6}
303.15	0.0567	5.75×10^{-6}
308.15	0.090	9.16×10^{-6}
313.15	0.137	1.40×10^{-5}
318.15	0.228	2.34×10^{-5}
323.15	0.365	3.77×10^{-5}
328.15	0.545	5.67×10^{-5}
	Cyclohexanone	
293.15	1.382	1.87×10^{-4}
298.15	1.485	2.01×10^{-4}
303.15	1.595	2.17×10^{-4}
308.15	1.702	2.33×10^{-4}
313.15	1.808	2.48×10^{-4}
318.15	1.937	2.67×10^{-4}
323.15	2.062	2.85×10^{-4}
328.15	2.181	3.03×10^{-4}

temp, K	solubility, g L^{-1}	temp, K	solubility, g L^{-1}
	0.5 M Aqueous Sodium Perchlorate Solution		
293.15	1.47×10^{-3}	313.15	4.67×10^{-3}
298.15	2.18×10^{-3}	318.15	5.80×10^{-3}
303.15	2.86×10^{-3}	323.15	6.85×10^{-3}
308.15	3.66×10^{-3}	328.15	7.57×10^{-3}
	1.0 M Aqueous Sodium Perchlorate Solution		
293.15	2.06×10^{-3}	313.15	6.85×10^{-3}
298.15	2.97×10^{-3}	318.15	8.26×10^{-3}
303.15	4.32×10^{-3}	323.15	9.66×10^{-3}
308.15	5.43×10^{-3}	328.15	10.43×10^{-3}
	2.0 M Aqueous Sodium Perchlorate Solution		
293.15	3.11×10^{-3}	313.15	1.24×10^{-2}
298.15	5.02×10^{-3}	318.15	1.45×10^{-2}
303.15	6.84×10^{-3}	323.15	1.53×10^{-2}
308.15	9.84×10^{-3}	328.15	1.63×10^{-2}
	4.0 M Aqueous Sodium Perchlorate Solution		
293.15	6.31×10^{-3}	313.15	2.69×10^{-2}
298.15	1.05×10^{-2}	318.15	3.15×10^{-2}
303.15	1.60×10^{-2}	323.15	3.34×10^{-2}
308.15	2.12×10^{-2}	328.15	3.53×10^{-2}

Table II. Solubilities of Mercury(II) Octadecanoate in Water at Various Temperatures

temp, K	10^3(solubility), g L^{-1}	pK_{SP}
293.15	0.669 ± 0.017	17.58 ± 0.05
298.15	0.867 ± 0.021	17.24 ± 0.04
303.15	1.146 ± 0.018	16.87 ± 0.04
308.15	1.403 ± 0.016	16.61 ± 0.04
313.15	1.762 ± 0.019	16.31 ± 0.04
318.15	2.224 ± 0.023	16.01 ± 0.03
323.15	2.839 ± 0.017	15.69 ± 0.03
328.15	3.185 ± 0.024	15.44 ± 0.03

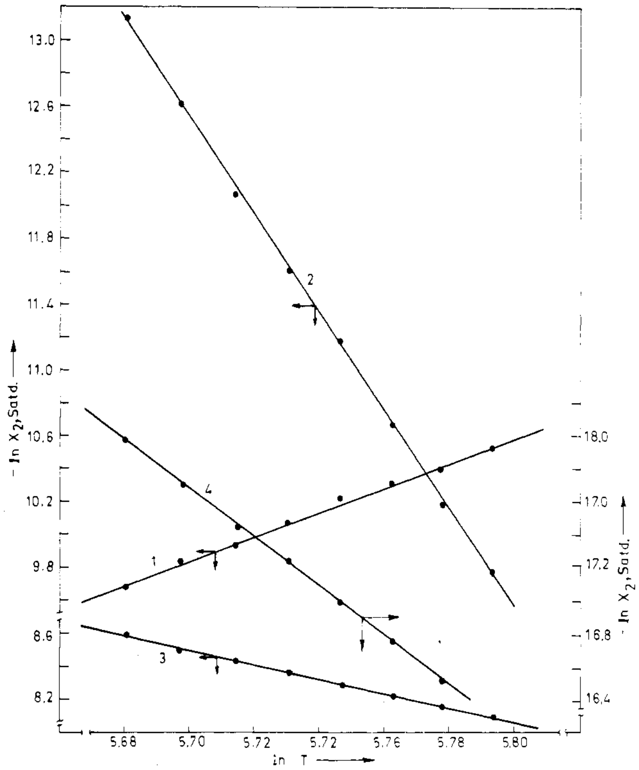

Figure 1. Solubility of MOD in various polar solvents: (1) formamide, (2) *N*,*N*-dimethylformamide, (3) cyclohexanone, (4) water.

were made for coincidence loss and the decay of the isotope. Replicate experiments showed practically no difference in the final solute concentrations. The maximum error in the solubility data reported by us is estimated to be around 1%.

Results and Discussion

The experimental values for the solubility (S) of MOD in aqueous solutions of sodium perchlorate and in formamide, *N*,*N*-dimethylformamide, and cyclohexanone over the temperature range 293–328 K are recorded in Table I. The term $X_{2,\mathrm{satd}}$ in the table refers to the mole fraction of solute in the saturated solution. Each data point reported by us is the mean of at least three replicates.

For aqueous solutions of sodium perchlorate, the plots of log S vs. (ionic strength)$^{1/2}$ yielded straight lines at every temperature of measurement. The solubilities of mercury(II) octadecanoate in water given in Table II have been obtained by extrapolating the linear plots to zero ionic strength. The solubility results are also shown as plots of ln $X_{2,\mathrm{satd}}$ vs. ln T in Figure 1. It is observed that the solubility of mercury(II) octadecanoate follows the order cyclohexanone > formamide > *N*,*N*-dimethylformamide ≫ water. MOD is only slightly soluble in water. Further, we find that the solubility of mercury(II) octadecanoate increases with increase of temperature in water, *N*,*N*-dimethylformamide, and cyclohexanone whereas in formamide it shows a slight decrease. No solubility values for MOD in these solvents have been reported in the literature to the best of our knowledge.

The plots of ln $X_{2,\mathrm{satd}}$ vs. ln T for all the systems yield straight lines in the studied temperature range. The linearity provides a check on the precision of measurements.

The entropy of dissolution of solids is given by the following thermodynamic relationship (*7*):

$$\Delta S = \bar{S}_2 - S_2^{\mathrm{s}} = -R(\partial \ln X_2/\partial \ln T)_{\mathrm{satd},P}(\partial \ln a_2/\partial \ln X_2)_{P,T} \quad (1)$$

The term $(\partial \ln a_2/\partial \ln X_2)_{P,T}$ in eq 1, which is the "Henry's law factor", approaches unity with increasing dilution. The quantity $-R(\partial \ln X_2/\partial \ln T)_{\mathrm{satd},P}$ can, therefore, be taken to represent $\bar{S}_2 - S_2^{\mathrm{s}}$, the entropy of solution of the solute in the solvent. From the slopes of the straight lines in Figure 1 the term $\Delta S[=-R(\partial \ln X_2/\partial \ln T)_{\mathrm{satd},P}]$ has been calculated and re-

Table III. Entropy of Solution (cal deg^{-1}) and Solubility of Mercury(II) Octadecanoate at 298.15 K

solvent	ΔS^a	$-R \ln X_{2,satd}$
formamide	−14.85	19.51
N,N-dimethylformamide	34.97	25.04
cyclohexanone	8.52	16.91
water	29.58	35.19

[a] $= -R[\partial \ln X_2/\partial \ln T]_{satd,P}$.

corded in Table III along with $-R \ln X_{2,satd}$ values at 298.15 K.

The entropy of solution can alternatively be obtained by dividing the process of transfer of solute from solid to saturated solution at constant temperature into three steps, viz., (i) fusion of solid solute, (ii) expansion of $(1 - X_{2,satd})/X_{2,satd}$ mol of solvent by a volume equivalent to $\bar{V}_2 - V_2°$, i.e., the difference in the partial molar volume of solute in the solvent $\bar{V}_2$ and the molar volume of pure liquid solute $V_2°$, and (iii) mixing the liquid solute and liquid solvent at constant volume, so that

$$\Delta S = \Delta S_{fusion} + \Delta S_{expan} + (\Delta S_{mix})_V$$

$$= \Delta S_{fusion} + (\bar{V}_2 - V_2°)(\partial P/\partial T)_V - R[\ln \phi_2 + \phi_1(1 - v_2°/v_1°)] \quad (2)$$

where ϕ_1 and ϕ_2 are the volume fractions of the solvent and the solute, respectively. When $X_{2,satd}$ is small, eq 2 can be rewritten as

$$\Delta S = \Delta S_{fusion} + (\bar{V}_2 - V_2°)(\partial P/\partial T)_V - R \ln X_{2,satd} - R[1 - v_2°/v_1° + \ln (v_2°/v_1°)] \quad (3)$$

For the systems under investigation, very low values for the term $\Delta S + R \ln X_2$ are obtained (Table III). The numerical value of the last term of eq 3 is expected to be between 2 and 6 cal deg^{-1} and therefore does not contribute significantly to this. Apparently ΔS_{expan} offers large negative contribution to the entropy of dissolution revealing that $\bar{V}_2 \ll V_2°$.

The data clearly indicate the existence of specific solute-solvent interactions resulting in either complexation or intermolecular bonding of MOD with the polar solvents. In highly polar solvents, namely, formamide, *N,N*-dimethylformamide, and cyclohexanone, the association effect of soap dipoles is expected to be considerably reduced and, as a result of this, solutions of unimolecular solute are obtained. The increased solubilities of MOD in these solvents may be a consequence of increased unimolecular solute-solvent interactions (*8*-*10*).

The results reported here shall be used along with other solution and surfactant properties of MOD to assess its applied utility.

Acknowledgment

We express our deep sense of gratitude to Dr. K. K. G. Menon, Research Director, Hindustan Lever Research Centre, Bombay (India), for providing the necessary facilities during the preparation of this manuscript.

Registry No. Mercury(II) octadecanoate, 645-99-8; dimethylformamide, 68-12-2; cyclohexanone, 108-94-1; water, 7732-18-5; formamide, 75-12-7.

Literature Cited

(1) Buono, F. J.; Feldman, M. L. In "Kirk—Othmer Encyclopedia of Chemical Technology", 3rd ed.; Martin, G., David, E., Eds.; Wiley: New York, 1979; Vol. 8, pp 34-49.
(2) Pilpel, N. *Chem. Rev.* **1963**, *63*, 221.
(3) Pilpel, N. *Manuf. Chem. Aerosol News* **1971** *42*, 37.
(4) Riddick, J. A.; Bunger, W. B. "Technique of Organic Chemistry: Organic Solvents", 3rd ed.; Wiley-Interscience, New York, 1970; Vol. II.
(5) Timmermans, J. "Physicochemical Constants"; Elsevier: Amsterdam, 1965.
(6) Glew, G. N.; Hildebrand, J. H. *J. Phys. Chem.* **1956**, *60*, 616.
(7) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L.; "Regular and Related Solutions"; Van Nostrand: New York, 1970.
(8) Malik, W. U.; Ahmed, S. I. *Kolloid Z. Z. Polym.* **1969**, *234*, 1045.
(9) Rudakoff, G. *Congr. Chem. Process. Petrol. Natur. Gas., Budapest* (*1965*) **1966**, 772-7.
(10) Malik, W. U.; Jain, A. K.; Jhamb, O. P. *J. Chem. Soc. A* **1971**, 1514.

Received for review May 23, 1983. Accepted September 14, 1983.

Adsorption of Binary Gaseous Mixtures of Ethylene–Ethane and Ethylene–Propylene on a Carbon Molecular Sieve

Tomoko Nakahara,* Mitsuho Hirata, George Amagasa, and Tsuneyoshi Ogura

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, Japan

The adsorption of two binary gaseous mixtures on a carbon molecular sieve (MSC-5A) was measured. The adsorption equilibrium data for the system of ethylene–ethane–MSC-5A were obtained at 30 °C and at pressures of 20, 50, and 100 mmHg. The adsorption for the system of ethylene–propylene–MSC-5A was measured at 1.4 (at 5, 10, and 30 mmHg), 30 (20 and 50 mmHg), and 50 (30 and 70 mmHg) °C. The selectivity for the heavy component from the mixture was observed in both systems. The heterogeneity of the surface of the adsorbent was quite evident at low pressures for the system of ethylene and propylene, but was not evident at any pressure for the system of ethylene and ethane.

In the adsorption of binary gaseous mixtures on a heterogeneous and microporous adsorbent the adsorbed amount of the heavier component of the two was always greater than the value predicted from the isotherms of the pure components (*1*, *2*). There is a need for systematic experimental data for the adsorption of mixtures on a microporous adsorbent in order to develop prediction and correlation methods. In this paper the adsorption equilibrium were measured at 30 °C and at 20, 50, and 100 mmHg for the system of ethylene–ethane–carbon molecular sieve (MSC-5A), and at 1.4 (at 5, 10, and 30 mmHg), 30 (20 and 50 mmHg), and 50 (30 and 70 mmHg) °C for the system of ethylene–propylene–MSC-5A.

Experimental Section

The experimental apparatus and the procedure were the same as those previously reported (*1*) except that an integrator