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SURFACE TENSIONS OF SOME MOLTEN DIVALENT METAL CARBOXYLATES

M. SOLA AKANNI *

Chemistry Department, University of Ife, Ile-Ife (Nigeria)

HUGH D. BURROWS

Departamento de Química, Universidade de Coimbra, 3049 Coimbra (Portugal)

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ABSTRACT

The surface tensions have been determined by capillary rise for the liquid phase of certain long-chain carboxylates of lead(II), zinc(II) and cadmium(II) at 400 K. The validity of the method has been checked in one case using the ring method. The magnitudes of the surface tensions are comparable to those of short chain-length aliphatic hydrocarbons, and are very much lower than those of molten inorganic salts, suggesting that the surface behaviour is dominated by the hydrocarbon chains. Surface tensions appear to increase slightly with chain length, and are higher in zinc elaidate and oleate than in zinc stearate, indicating the importance of unsaturation. Surface tensions for cadmium soaps are somewhat lower than those of lead and zinc, possibly due to the different aggregates present in the melts. Parachors have been calculated using surface tension and molar volume data, and are found to be consistently lower than those predicted from atomic parachor parameters. Similar behaviour has previously been noted with many metal organic systems. Parachors of lead and zinc soaps are found to be linear functions of chain length, and the contribution to the parachor by the hydrophilic portion of the amphiphile is closer to the theoretical value for zinc(II) than lead(II), possibly due to the more covalent character of zinc(II) soaps.

INTRODUCTION

The divalent metal carboxylates (soaps) of long-chain fatty acids have many important applications [1], and a number of studies have been reported on the thermal behaviour [2–7], and both transport [8–14] and microscopic [6,15–17] properties of these systems. However, in spite of the importance of the interfacial behaviour of these compounds on such properties as their mold release ability in polymer processing [1], little has been presented on their surface or interfacial tensions. A few reports exist on the

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* To whom all correspondence should be addressed.

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surface tension of solutions of soaps of calcium, magnesium [18] and cadmium [19]. Whilst interfacial tensions of these systems are somewhat difficult to measure, they can be estimated from surface tension data [20].

Our interest in the thermal behaviour and transport properties of divalent metal soaps [5] has led us to investigate the surface tensions of the liquid phase of these systems. Results of this study are reported here.

EXPERIMENTAL

Preparation, purification and characterization of the soaps of lead [8], zinc [8,12], cadmium [10], mercury [11], copper [15] and manganese [13], and basic lead dodecylsulphate [21] have been reported previously.

Surface tensions were determined in contact with air by the capillary rise method [20,22–24] using clean, melting point capillaries of ca. 0.4 mm radius. Samples were contained in test tubes and slowly heated to just above the melting point in a liquid paraffin bath before introducing the capillaries. Capillary rises (h) were determined with a travelling microscope, and confirmed by quickly cooling the samples and measuring the lengths of solidified compounds. Normally, at least three measurements were made with each system. Capillary radii (r) were determined by filling with mercury, determining the mass and length of the mercury columns, and using the literature density of mercury [25]. Capillary rises were found to show no significant temperature dependence within the somewhat limited accuracy of our measurements. Surface tentions (γ) were calculated using the relation [22]

$$\gamma = \frac{\frac{1}{2}(\rho_1 - \rho_2)grh}{\cos\theta} \tag{1}$$

where ρ_1 and ρ_2 are the densities of sample and air, respectively, and θ is the contact angle. As has previously been assumed in related systems, such as fused sodium polysulphides [26], contact angles were assumed to be zero. Visual examination of the systems using a travelling microscope indicated that this assumption is reasonable within the accuracy ($\pm 10\%$) of our measurements. Densities and capillary rises were determined, and surface tensions calculated, at 400 K. A value of 0.9 kg m^{-3} was taken [25] for the density of air at this temperature.

The surface tension of molten lead tetradecanoate was also determined by the ring method [20,22,27] using a Pt–Ir ring (Krüss GmbH) of 1 cm diameter and a DuNoüy tensiometer (Cambridge Instrument Co. Ltd.). The sample was melted, and triplicate measurements were made of the tension at which the ring broke the surface. Whilst accurate temperature control was not possible in this case, measurements were made close to the melting point of the soap. The system was calibrated using n-hexane, and surface tension calculated using the ring method correction in ref. 27 for an *R/r* value of 50.

RESULTS AND DISCUSSION

Surface tensions in contact with air were determined by capillary rise for the liquid phase of certain even chain-length carboxylates of zinc(II), cadmium(II) and lead(II), and are reported in Table 1. The melts of manganese(II) dodecanoate, copper(II) dodecanoate and basic lead(II) dodecylsulphate were found to be too viscous to show any significant capillary rise. Capillary rises were also determined for the decanoate, dodecanoate, tetradecanoate and hexadecanoate of mercury(II), and were found to be close to those of the corresponding cadmium soaps. However, it was not possible to determine densities, and hence surface tensions, of these systems due to their thermal instability just above the melting point [11,28]. The accuracy of the capillary rise measured for the molten mercury soaps is also restricted due to the same effect.

TABLE 1

Densities, capillary rises and surface tensions of some molten soaps at 400 K

Compound	Density (10^3 kg m^{-3}) [a]	Capillary rise (mm) [b]	Surface tension (mN m^{-1})
Lead decanoate	1.3589	5	12.6
Lead dodecanoate	1.3006	5	12.1
Lead tetradecanoate	1.2218	7	15.9
Lead hexadecanoate	1.1691	7	15.2
Lead octadecanoate	1.1385	7	14.8
Zinc octanoate	1.0576	7	13.7
Zinc dodecanoate	0.9677	6	10.8
Zinc hexadecanoate	0.9393	7	12.2
Zinc octadecanoate	0.9254	5 [c]	13.6
Cadmium decanoate	–	small	–
Cadmium dodecanoate	1.1082	3	6.2
Cadmium hexadecanoate	1.0340	6	11.5
Zinc oleate	0.9838	10	18.2
Zinc elaidate	0.9564	11	19.5
Mercury decanoate	[d]	7	–
Mercury dodecanoate	[d]	6	–
Mercury tetradecanoate	[d]	3 [e]	–
Mercury hexadecanoate	[d]	5	–

[a] Calculated from data in refs. 8, 10 and 12.

[b] ±0.5 mm.

[c] Melt observed to be turbid.

[d] Not available due to decomposition above melting point.

[e] melt decomposes just above melting point.

For lead(II) tetradecanoate, the surface tension was also determined just above the melting point by the ring method. A value of $\gamma = 13.8$ mN m^{-1} was obtained, in reasonable agreement with the capillary rise value, given the limited accuracy of our measurements.

The magnitudes of the observed surface tensions are relatively close to those observed for short chain-length aliphatic hydrocarbons, such as hexane ($\gamma = 18.4$ mN m^{-1} at room temperature [29]), rather lower than those observed for oleic acid (32.5 mN m^{-1} [29]) or aliphatic alcohols such as octanol (27.5 mN m^{-1} [29]), and very much lower than for molten inorganic salts (a value of 105 mN m^{-1} has been reported for $PbCl_2 \cdot KCl$ at 471 ° C [30]). In spite of the somewhat limited accuracy of the measurements, there appears to be a definite trend of increasing γ with chain length. This is similar to what has been observed in aliphatic hydrocarbons, and suggests that the surface behaviour of the molten soaps is dominated by factors associated with the hydrocarbon chains. The surface tensions of the molten oleate and elaidate of zinc(II) are significantly higher than those of the octadecanoate, indicating the effect of unsaturation. Whilst it is difficult to find literature for comparison, the surface tension of the glyceride triolein (29.3 mN m^{-1} at 99.8 ° C) is rather higher than that of tristearin (26.8 mN m^{-1} at 100 ° C [31]), indicating that similar factors are involved.

Whilst the surface tensions of similar chain-length lead(II) and zinc(II) soaps are very close, those of the corresponding cadmium(II) soaps appear to be somewhat lower. This may be associated with differences in the micellular aggregates in the molten systems. Viscosity and DTA data show that lead(II) and zinc(II) soaps have fairly small aggregates [9,32,33], whereas molten cadmium(II) soaps appear to have rather larger, cylindrical aggregates [10,33].

TABLE 2

Experimental and calculated parachors of some molten soaps of lead(II), zinc(II) and cadmium(II)

Compound	$\|P\|$ experimental	$\|P\|$ calculated
Lead decanoate	762.3	948.4
Lead dodecanoate	868.6	1104.4
Lead tetradecanoate	1081.9	1260.4
Lead hexadecanoate	1212.2	1416.4
Lead octadecanoate	1333.5	1572.4
Zinc octanoate	639.8	766.9
Zinc dodecanoate	868.0	1078.9
Zinc hexadecanoate	1145.3	1390.9
Zinc octadecanoate	1310.0	1546.9
Zinc oleate	1382.4	1524.9
Zinc elaidate	1387.8	1524.9
Cadmium dodecanoate	726.8	1092.2
Cadmium hexadecanoate	1079.7	1410.2

Surface tensions and molar volumes (V_m) of a substance at a given temperature can be used [34–36] to calculate Sugden's parachor parameter $|P|$

$$|P| = V_m\gamma^{0.25} \tag{2}$$

which has been suggested to be primarily an additive and constitutive property. Using literature values for the molar volumes of lead(II) [8],

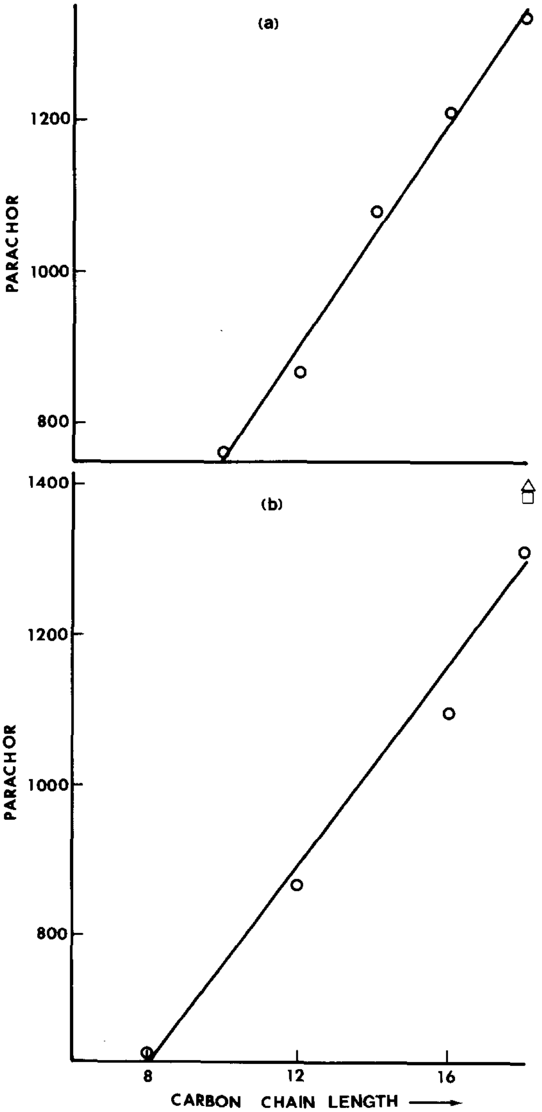

Fig. 1. Plots of experimental parachor values versus carbon chain length for carboxylates of: (a) lead(II); (b) zinc(II). Also included in (b) are values for zinc(II) oleate (□) and elaidate (△).

zinc(II) [8,12] and cadmium(II) [10] carboxylates, the parachors have been determined at 400 K. These are compared in Table 2 with values calculated on an additive basis using atomic and bond parachors from ref. 35. Whilst the correct trend is observed, the calculated values are consistently higher than the experimental ones. Similar discrepancies between experimental and calculated values have been noted with several organometallic compounds [35,36]. Plots of experimental parachor against carbon chain length are linear for the lead(II) (correlation coefficient 0.9943) and zinc(II) (correlation coefficient 0.9976) soaps (Fig. 1). Extrapolation of the data for $(H(CH_2)_nCO_2)_2M$ to $n = 0$ in the two cases gives a value close to that expected from the atomic parachor parameters in the zinc(II) case ($|P|_{n \to 0} = 156.6$; $|P|_{ZnC_2H_2O_4} = 174.5$), but much lower in lead(II) ($|P|_{n \to 0} = 85.8$; $|P|_{PbC_2H_2O_4} = 200$). Theoretical parachor values assume totally covalent bonds, and it is possible that the discrepancy in the lead(II) case results from this ion being relatively more ionic in the melt than zinc(II), as has been suggested from conductance measurements [8].

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