Thermochimica Acta, 54 (1982) 289–296
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THE DENSITIES AND MOLAR VOLUMES OF MOLTEN LEAD(II) DODECANOATE/DODECANOIC ACID MIXTURES OVER THEIR COMPLETE COMPOSITION RANGE: EVIDENCE FOR NON-IDEAL BEHAVIOUR

M. SOLA AKANNI, HUGH D. BURROWS *, FOLUSADE OSHODI and H. CHARLES SINE
Department of Chemistry, University of Ife, Ile-Ife (Nigeria)

(Received 26 October 1981)

ABSTRACT

Data are presented for the densities and molar volumes of the molten system lead(II) dodecanoate/dodecanoic acid over its complete composition range. For equimolar mixtures, plots of molar volume against temperature show curvature at high temperatures, suggesting deviations from ideal behaviour. Support for this comes from a plot of molar volume at constant temperature against acid mole fraction. Densities and molar volumes are reported for lead (II) carboxylate/carboxylic acid (0.5 mole fraction) and for pure carboxylic acid for the even chain acids C_{10} to C_{18}. The molar volumes at constant temperature in these cases are linear functions of chain length, although the volume occupied per methylene group in equimolar mixtures is suggested to be slightly smaller than with pure soap or pure acid. An explanation for non-ideal behaviour becoming more marked at higher temperature is given in terms of acid monomer–dimer equilibria.

INTRODUCTION

Long chain lead(II) carboxylates exhibit a liquid phase consisting of micellar aggregates between their melting points (around 400 K) and their decomposition temperatures (typically above 510 K). Information on the nature of aggregation has been obtained by thermal analysis [1] and by the study of such physical properties as density, viscosity, and electrical conductivity of the molten carboxylates [2,3]. It is suggested that the liquid phase consists of small, spherical micelles containing 3–5 soap molecules [1,3]. Studies have been made of the effect of various additives (up to 0.2 mole fraction) on the phase behaviour and physical properties of the systems. Whilst addition of lead(II) oxide to the carboxylates appears to favour a change in structure of the soap aggregates into long, cylindrical micelles [4,5], addition of lead(II) acetate [6,7], or long chain carboxylic acids [8,9] did not significantly affect the state of aggregation of the soap in the liquid phase. It is of interest to obtain information on the liquid phases of these binary systems over a wider composition range to see whether they behave ideally, or whether one component may affect the

---

* To whom all correspondence should be addressed.

aggregation of the other. We have chosen to examine the densities and molar volumes of the system lead(II) dodecanoate/dodecanoic acid in detail, as the liquid phases of the two components are stable over similar temperature ranges and appear to be completely miscible from optical observation. Earlier work [9] has indicated that, whilst at constant temperature plots of molar volume vs. composition are linear for this system up to 0.2 mole fraction, there might be slight deviations from ideal behaviour at higher acid concentrations.

EXPERIMENTAL

Preparation and/or purification of lead(II) carboxylates, carboxylic acids and their mixtures have previously been described in detail [1,8,9]. Densities were measured using a glass pyknometer in a furnace. Since studies of non-ideal behaviour involve the determination of very small differences between two or more very large quantities, they are very sensitive to any errors in these terms. The pyknometer was calibrated with mercury, and corrections were made for thermal expansion of the glass [2]. The major source of error in the present system occurs in the temperature control and measurement. A mercury-in-glass thermometer was used with its bulb adjacent to the pyknometer. Whilst the thermometer had been standardized to ±0.3°C, the actual error of temperature measurement was likely to be $\leqslant \pm 1$°C. The precision of temperature measurement was rather better than this and attempts were made to minimise the temperature errors by making measurements over a wide temperature range and averaging the data.

RESULTS

Densities and molar volumes were determined of lead(II) dodecanoate/dodecanoic acid mixtures over the composition range from pure soap to pure acid. Plots of densities and molar volumes against temperature were linear at all compositions except 0.5 and 0.6 mole fraction of acid. In these two cases, slight but significant curvature was observed at higher temperatures. The curve for $\chi_{\mathrm{acid}} = 0.60$ is shown in Fig. 1. The densities were fitted by least squares to the equation

$$\rho_T = \rho_0 - aT \qquad (1)$$

and molar volumes to

$$V_m(T) = V_0 + bT \qquad (2)$$

where a and b are constants. For 0.5 and 0.6 mole fractions of acid, only low temperature data was used for the fit. The parameters determined by least squares analysis, together with their standard errors and range of measurement, are presented in Table 1.

At any particular temperature, both the densities and molar volumes show a steady decrease with increasing mole fraction of acid. However, plots of molar

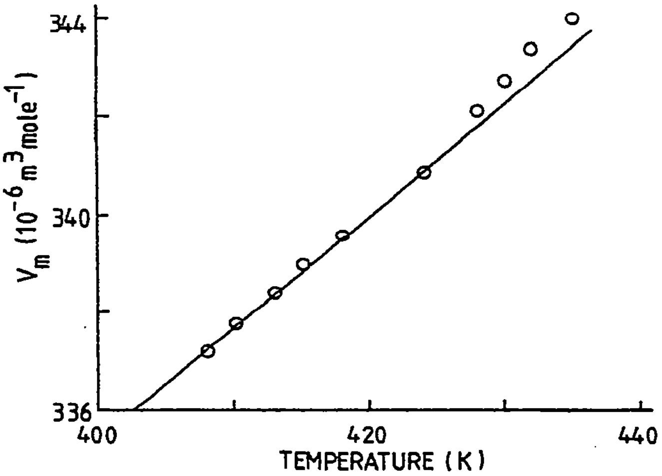


Fig. 1. Plot of molar volume against temperature for the system lead(II) dodecanoate/dodecanoic acid (0.6 mole fraction). The straight line is the low temperature least squares slope.

volume against mole fraction at constant temperature showed slight, but statistically significant deviations from linearity. These become more marked with increasing temperature. The plot for 430 K, together with the standard errors of the individual points, is shown in Fig. 2. The straight line is the least squares slope for data at

TABLE 1

Densities and molar volumes of lead(II)dodecanoate/dodecanoic acid mixtures

X_{acid}	Temp. range (K)	$\rho=\rho_0-aT$ (10^3 kg m^{-3})				$V_m=V_0+bT$ (10^{-6} m^3 mole^{-1})			
		ρ_0	Stnd. error (%)	$a\times 10^3$	Error in a (%)	V_0	Stnd. error (%)	b	Error in b (%)
0.00	421–471	1.680	0.08	0.89	3.4	330.3	0.15	0.330	3.1
0.06	398–442	1.654	0.70	0.90	3.3	320.0	0.15	0.320	3.5
0.10	407–448	1.692	0.77	1.00	3.0	295.2	0.15	0.354	3.0
0.20	420–480	1.603		0.82		296.7		0.288	
0.30	388–447	1.485	0.33	0.67	1.5	304.8	0.62	0.230	1.7
0.35	393–416	1.711		1.33		218.4		0.425	
0.40	377–422	1.523	0.94	0.84	6.1	268.0	0.75	0.266	2.0
0.45	387–429	1.471		0.79		264.1		0.259	
0.50	387–441	1.450	0.71	0.78	3.2	256.9	0.37	0.244	1.0
0.55	383–429	1.405		0.72		253.6		0.225	
0.60	408–470	1.406	0.28	0.78	1.3	232.2	0.67	0.247	1.2
0.65	363–402	1.419		0.90		215.6		0.271	
0.70	369–422	1.435	0.55	1.03	1.8	188.5	1.28	0.317	1.8
0.80	361–407	1.240		0.68		209.1		0.202	
0.85	373–387	1.298	0.23	1.00	0.1	170.8	0.69	0.272	1.1
0.90	374–473	1.218	0.59	0.72	4.2	176.0	0.90	0.217	1.9
1.00	334–411	1.005	0.19	0.40	0.1	193.0	0.29	0.110	7.4

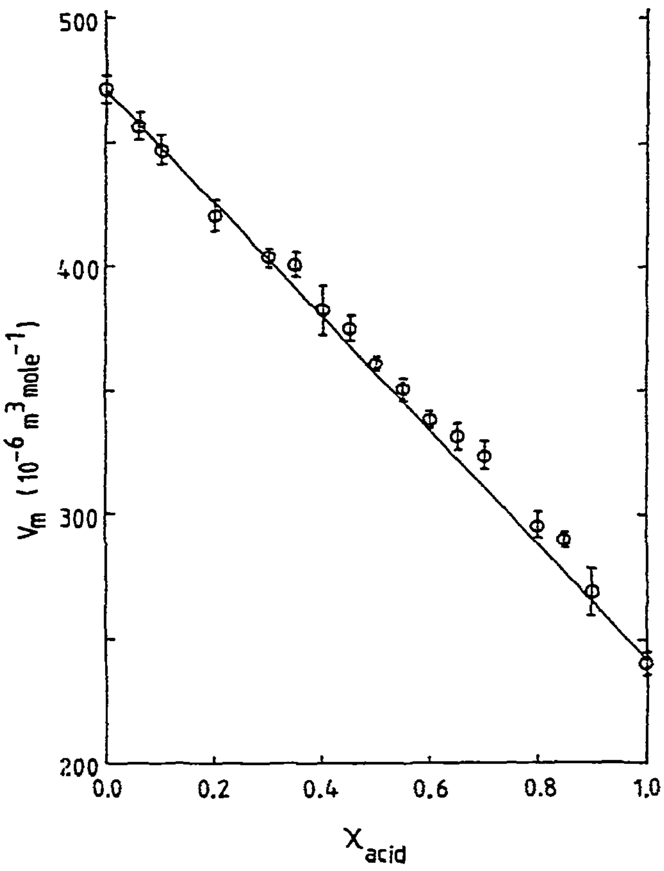


Fig. 2. Plot of molar volume at 430 K vs. acid mole fraction for the system lead(II) dodecanoate/dodecanoic acid.

$\chi_{acid} \leqslant 0.1$, and $\chi_{acid} \geqslant 0.9$, using values from the present study and from ref. 9.

It thus appears that, as suspected from extrapolation of data for the lead(II) dodecanoate/dodecanoic acid systems at low acid mole fractions [9], there is slight but significant positive deviation from ideality. The limited accuracy of our method does not permit determination of meaningful excess volumes of mixing, although the present data suggests that they lie in the range $(5-10) \times 10^{-6}$ m^3 $mole^{-1}$ at 0.5 mole fraction of acid.

To obtain further information on the interactions occurring in the system, densities and molar volumes were determined for the system lead(II) carboxylate/carboxylic acid (0.5 mole fraction) and for pure carboxylic acids for the even chain length acids C_{10} to C_{18}. For the systems lead(II) hexadecanoate/hexadecanoic acid (0.5 mole fraction) and lead(II) octadecanoate/octadecanoic acid (0.5 mole fraction), as in the corresponding lead(II) dodecanoate/dodecanoic acid system, slight curvature was observed in plots of molar volume against temperature. The data was fitted by least squares to eqns. (1) and (2), with the low temperature data only being used for the C_{16} and C_{18} systems. The parameters for the mixtures, and for the pure acids are presented in Tables 2 and 3, respectively. The densities for

TABLE 2

Densities and molar volumes of lead(II)carboxylate/carboxylic acid (0.5 mole fraction) systems

Carbon chain length	Temp. range (K)	$\rho=\rho_0-aT$ (10^3 kg m^{-3})				$V_m=V_0+bT$ (10^{-6} m^3 mole^{-1})			
χ(%)		ρ_0	Stnd. error (%)	$a\times10^3$	Error in a (%)	V_0 (%)	Stnd. error (%)	b	Error in b (%)
10	362–378	1.642	1.02	1.15	3.7	192.93	0.10	0.279	1.4
12	387–409	1.384	0.71	0.62	3.2	279.64	0.37	0.188	1.1
14	373–389	1.422	0.83	0.88	3.4	281.80	1.7	0.335	3.3
16	375–390	1.329	1.04	0.74	4.1	344.62	1.8	0.316	4.7
18	380–397	1.373	1.08	0.77	3.9	355.00	2.1	0.354	5.1

TABLE 3

Densities and molar volumes of even chain length carboxylic acids

Carbon chain length	Temp. range (K)	$\rho=\rho_0-aT$ (10^3 kg m^{-3})				$V_m=V_0+bT$ (10^{-6} m^3 mole^{-1})			
		ρ_0	Stnd. error (%)	$a\times10^3$	Error in a (%)	V_0 error	Stnd. error (%)	b	Error in b (%)
10	302–324	1.070	0.27	0.61	1.6	150.88	0.94	0.142	2.8
12	334–411	1.005	0.19	0.40	0.1	193.00	0.29	0.110	7.4
14	337–358	1.064	0.37	0.64	1.6	200.68	0.48	0.201	1.0
16	352–369	1.077	0.37	0.69	1.4	214.41	0.50	0.264	0.8
18	359–373	1.118	0.09	0.79	0.4	223.23	0.30	0.325	0.6

pure acids are in reasonable agreement with literature values [10].

At constant temperature, the molar volumes for both the mixtures and the pure acids were found to be reasonably linear functions of carbon chain length. The data at 430 K were fitted by least squares to the equations

$$V_m(430) = (61.33 + 25.43\,n) \times 10^{-6}\ \text{m}^3\ \text{mole}^{-1} \tag{3}$$

for the system lead(II) carboxylate/carboxylic acid (0.5 mole fraction) and

$$V_m(430) = (13.26 + 19.49\,n) \times 10^{-6}\ \text{m}^3\ \text{mole}^{-1} \tag{4}$$

for the pure carboxylic acids, where n is the total carbon chain length of the acid. Correlation coefficients were greater than 0.99 in both cases. As with previous studies on the pure soaps [1,11], it can be noted that the total number of carbon atoms per soap molecule is $2n$, whereas the total number of carbon atoms per acid molecule is n. For the 0.5 mole fraction mixture, taking $n = 1.5$ gives an increase in volume per methylene group of $16.96\ (\pm 0.95) \times 10^{-6}\ \text{m}^3\ \text{mole}^{-1}$, which appears to be slightly smaller than that of pure acid ($19.49 \pm 0.77 \times 10^{-6}\ \text{m}^3\ \text{mole}^{-1}$), or pure soap ($17.95 \pm 0.01 \times 10^{-6}\ \text{m}^3\ \text{mole}^{-1}$ [12]) under the same conditions.

DISCUSSION

Results from thermal analysis [1], electrical conductivity [2], and viscosity [3] indicate that molten long chain lead(II) carboxylates consist of aggregates having 3–5 soap molecules. In contrast, the corresponding long chain carboxylic acids have a liquid phase consisting predominantly of hydrogen bonded dimers [13–15]. It is of interest to see whether the carboxylic acid moieties will affect the structures of the corresponding lead(II) soap aggregates. Extrapolation of data for low acid mole fraction lead(II) dodecanoate/dodecanoic acid systems does provide some evidence for non-ideal behaviour on mixing [9]. Further evidence is found in the present study. Firstly, whilst low or high acid mole fraction mixtures show the expected linear plots of molar volume against temperature, at $\chi_{\text{acid}} \simeq 0.5$ these plots show curvature at high temperatures. In addition, whilst with our present experimental set-up it is not possible to determine precise values of excess volumes, plots of molar volume at constant temperature against mole fraction for the system lead(II) dodecanoate/dodecanoic acid show deviations from purely additive behaviour which are greater than the experimental errors. Some further support for non-ideal behaviour comes from the study of the molar volumes of various even chain length lead(II) carboxylate/carboxylic acid systems. With the hexadecanoate and octadecanoate mixtures at $\chi_{\text{acid}} \simeq 0.5$, again curvature was observed in the plots of molar volume against temperature. Further, by studying molar volume at constant temperature as a function of chain length it is possible to estimate the volume occupied per methylene group. The data at 430 K for 0.5 mole fraction mixtures suggests that this is slightly smaller for the mixture than for pure acid or pure soap. Extrapolation of the data [9] for lead(II) carboxylate/carboxylic acid (0.1 mole fraction) to the same temperature gives a volume per methylene group (17.31×10^{-6} m^3 mole^{-1}) intermediate between that of pure soap and the 0.5 mole fraction system.

Additional evidence for non-ideal behaviour can be gained from reconsideration of previously reported viscosity data for the lead(II) dodecanoate/dodecanoic acid system [9]. For ideal mixtures at constant temperature, the product of the viscosity and the molar volume of the mixture can be related [16] to those of the pure components by

$$\ln \eta_s V_{m_s} = \chi_a \ln \eta_a V_{m_a} + \chi_b \ln \eta_b V_{m_b} \tag{5}$$

where subscripts s, a, and b refer to the mixture and pure components, respectively. Experimental values at 430 K of $\ln \eta\ V_m$ for low acid mole fraction mixtures, and values calculated according to eqn. (5) are shown in Fig. 3. Again, deviations from ideal behaviour are greater than the maximum error limits for certain acid mole fractions. Whilst there is no simple correlation between non-ideal behaviour in a thermodynamic sense and non-ideal behaviour in viscosities of solution [16], these results do tend to reinforce the view that the system lead(II) dodecanoate/dodecanoic acid behaves non-ideally.

Deviations from ideal behaviour in the present system presumably arise from changes in the nature of the aggregates present in solution. Viscosity data [9] has indeed shown a decrease in size of the lead(II) carboxylate units of flow upon addition of the corresponding carboxylic acid. It is worth noting that with reversed micellar systems [17], whilst addition of water favours increased aggregation, the presence of other additives frequently leads to a reduction in the tendency to micellize as a consequence of a resistance to mixing.

It is seen in the present study that deviations appear to become more marked with

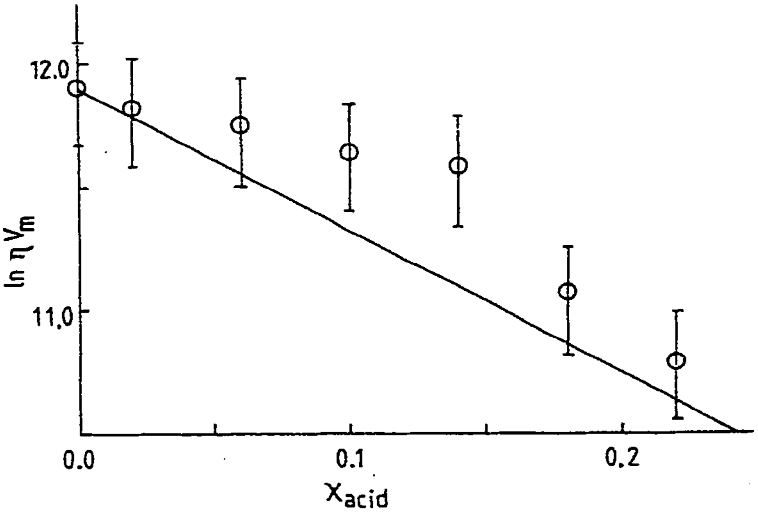
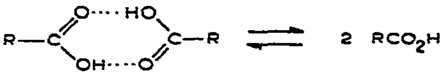


Fig. 3. Plot of $\ln \eta\ V_m$ vs. acid mole fraction for the system lead(II) dodecanoate/dodecanoic acid at 430 K. The circles are experimental points with maximum error limits. The straight line is calculated for an ideal mixture using eqn. (5).

increasing temperature. For example, plots of V_m against temperature for equimolar compositions tend to become non-linear at higher temperatures. This can be rationalised by considering the monomer–dimer equilibria of the molten carboxylic acids.



(6)

Thermodynamic data [13] on dodecanoic acid, for example, indicates that over the temperature range looked at in this study the monomer concentration increases with temperature, and by 430 K more than 30% of the acid is present as the monomer. Monomeric acid species would be much more likely to disturb the soap aggregates than the hydrogen bonded dimers, such that deviations from ideal behaviour would tend to increase with increasing temperature. It is noteworthy that the highest degree of dissociation of acid dimers is observed with dodecanoic, hexadecanoic and octadecanoic acids [13], and that the plots of V_m against temperature for the corresponding lead(II) carboxylate/carboxylic acid (0.5 mole fraction) systems all show curvature. In contrast, with the less dissociated decanoic and tetradecanoic acids, plots of molar volume against temperature are linear for equimolar soap/acid mixtures. The reason for the behaviour of the acid monomer–dimer equilibrium not being a simple function of chain length of the acid is not immediately obvious. However, our results on the molar volume behaviour of these soap/acid systems do lend qualitative support to the work of Sime et al. [13].

REFERENCES

1 S.O. Adeosun and S.J. Sime, Thermochim. Acta, 17 (1976) 351.
2 M.E. Ekwunife, M.U. Nwachukwu, F.P. Rinehart and S.J. Sime, J. Chem. Soc. Faraday Trans. 1, 71 (1975) 1432.
3 U.J. Ekpe and S.J. Sime, J. Chem. Soc. Faraday Trans. 1, 72 (1976) 1144.
4 S.O. Adeosun, W.J. Sime and S.J. Sime, Thermochim. Acta, 19 (1977) 275.
5 S.O. Adeosun, M.S. Akanni and H.D. Burrows, Thermochim. Acta, 42 (1980) 233.
6 S.O. Adeosun, Thermochim. Acta, 25 (1978) 333.
7 S.O. Adeosun, Thermochim. Acta, 32 (1979) 119.
8 S.O. Adeosun and M.S. Akanni, Thermochim. Acta, 27 (1978) 133.
9 S.O. Adeosun and M.S. Akanni, Thermochim. Acta, 39 (1980) 35.
10 Handbook of Chemistry and Physics, CRC Press, Cleveland, OH, 57th edn., 1976–77, pp. C271–C512.
11 S.O. Adeosun, W.J. Sime and S.J. Sime, J. Chem. Soc. Faraday Trans. 1, 72 (1976) 2470.
12 Calculated from data in ref. 2.
13 S.J. Sime, W.J. Sime, R.A.N. McLean and M.V. Olaoye, Niger. J. Science, 10 (1976) 267.
14 D.S. Sarkadi and J.H. DeBoer, Recl. Trav. Chim. Pays-Bas, 76 (1957) 628.
15 L.W. Reeves, Trans. Faraday Soc., 55 (1959) 1684.
16 T.M. Reed and T.E. Taylor, J. Phys. Chem., 63 (1959) 58.
17 J.H. Fendler, Acc. Chem. Res. 9 (1976) 153.