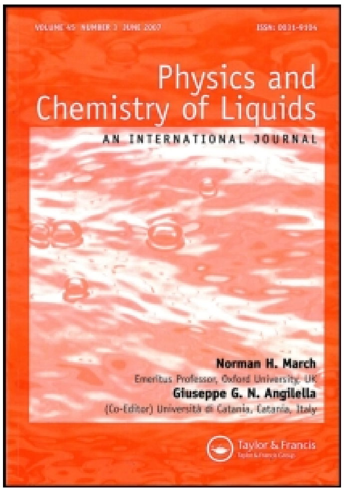

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Saar, J. and Ruppersberg, H.(1987) 'Density, Compressibility, Heat Capacity and Surface Tension of Liquid Li/Ba Alloys', Physics and Chemistry of Liquids, 17: 1, 45 — 53
To link to this Article: DOI: 10.1080/00319108708078540
URL: http://dx.doi.org/10.1080/00319108708078540

Phys. Chem. Liq., 1987, Vol. 17, pp. 45–53
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Printed in the United Kingdom

Density, Compressibility, Heat Capacity and Surface Tension of Liquid Li/Ba Alloys

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(Received 30 November 1986)

Density ρ, compressibility χ_S and surface tension Γ, of liquid Li/Ba alloys have been measured at various compositions as a function of temperature. The heat capacity C_p was determined at 400 K. The variation of the molar volume V and of Γ with composition c is almost linear. $\chi_T(c)$ and $\chi_S(c)$ are S-shaped, $C_p(c)$ and $C_v(c)$ have positive excess values.

Key words: Thermodynamic properties, liquid Li/Ba alloys.

1 INTRODUCTION

The investigation of liquid Li/Ba alloys presented in this paper is part of a program to study the influence of atomic size differences on the properties of simple liquid binary alloys. The ratio $\beta = V_1/V_2$ of the molar volumes of the constituents taken at their melting temperature amounts to 0.33. The larger atoms being labelled "2" throughout this paper. Similar studies are on the way for Li/Sr and Li/Ca with $\beta = 0.39$ and 0.46, respectively. Li systems are investigated because they allow to reveal structural features which are especially interesting for comparison with theoretical structure data: neutron diffraction pattern pronounce the effect of concentration fluctuations and discriminate most strongly between equal and unequal atomic pairs whereas the mutual distribution of the non-lithium constituents dominates the X-ray diffraction pattern of alloys with not too high Li content. Neutron diffraction data of liquid Li/Ba are discussed by one of us (Ruppersberg[1]) in a separate paper where also a brief description of current thermodynamic methods is given, together with their application to Na/Cs which is the most thoroughly studied system of this type and for which $\beta = \frac{1}{3}$. The relevant equations for ΔF, the free energy of mixing are the Flory–Huggins equation (FH):

$$\Delta F_{\mathrm{FH}} = RT(c_1 \ln \Phi_1 + c_2 \ln \Phi_2) - \omega c_1 \Phi_2 \qquad (1)$$

with the (idealized) volume fractions $\Phi_i = c_i V_i/(c_1 V_1 + c_2 V_2)$, $(i = 1, 2)$, and the interchange energy ω. For hard sphere (HS) mixtures the use of the Mansoori equation is recommended (see Shimoji[2]):

$$\Delta F_{\mathrm{HS}} = -T(\Delta S_{\mathrm{gas}} + S_c + \Delta S_\eta + S_\sigma) \qquad (2)$$

where ΔS_{gas} represents the ideal gas entropy, S_c is the entropy of ideal mixing. The terms ΔS_η and S_σ are contributions of packing and misfit, respectively, for which explicit formulae in terms of the packing fraction η and the hard sphere diameters σ_i are available[3,4]. The mixing entropy of athermal hard-sphere mixtures ΔS^a_{HS}, is given by $-\Delta F_{\mathrm{HS}}/T$. If however η and σ vary with temperature then

$$\Delta S_{\mathrm{HS}} = -(\partial \Delta F_{\mathrm{HS}}/\partial T)_v = \Delta S^a_{\mathrm{HS}} + T((\partial \Delta S_\eta/\partial T)_v + (\partial S_\sigma/\partial T)_v). \qquad (3)$$

$(\partial\eta/\partial T)_v$ which is needed for calculating ΔS_{HS} is obtained by differentiating

$$\eta = \eta_1 + \eta_2 = \pi\rho_0(c_1\sigma_1^3 + c_2\sigma_2^3)/6 \qquad (4)$$

where $\rho_0 = N/V$ is the mean number density, and which yields $(\partial\eta/\partial T)_v = (\partial\eta/\partial T)_p + \eta\cdot(\partial V/\partial T)_p/V$ assuming σ independent of V. Values of η_i and σ_i and of their temperature derivatives have been obtained from structure data of pure liquid Li and Ba[1].

For liquid metals a refinement of the HS model is possible by introducing a uniform background potential u_g which for alloys yields an energy of mixing ΔE, to be added to ΔF_{HS} of Eq. (2). Approximate equations to calculate u_g and ΔE are given in Shimoji's book[2], we will use the equations 109,4 and 205,2, respectively. In the discussion of the Na/Cs system the interchange term $-\omega c_1 \Phi_2$ of the FH equation was added by several authors to ΔF_{HS}, Eq. (2), to allow for an interaction between the hard spheres.

The structure data of Li/Ba alloys may quite well be approximated by HS curves[1]. Significant deviation from HS behaviour is observed for intermediate distances in r-space and for the long wavelength concentration fluctuations. The latter indicate a tendency for segregation and for alloys rich in lithium a positive interchange energy could be obtained from the FH Eq. (1).

Almost nothing is known about other properties of Li/Ba. Two phase diagrams which look quite different were published by Keller *et al.*[5] and

Haase[6], respectively. The first authors report an eutectic composition on the Li-side at about 10 at % Ba followed by the incongruently melting intermetallic compound $BaLi_4$. According to Haase the eutectic is at about 20 % Ba and incongruently melting compounds occur at $LiBa_2$ and $LiBa_6$. At the former composition the liquidus temperature exceeds the one reported by Keller *et al.* by about 100 K. For the solids no mutual solubility was detected.

2 EXPERIMENTAL

The samples were prepared inside a dry box under high purity argon from 99.9 % Li and 99.5 % Ba and the composition was checked by chemical analysis. The density ρ was measured in the same dry box using the maximum bubble pressure apparatus as described by Ruppersberg and Speicher[7]. Linear regression of the $\rho(T)$ curves yields $(\partial\rho/\partial T)_p$. In Table 1 are given the compositions, the temperature ranges, ρ at the liquids temperature and $(\partial\rho/\partial T)_p$. Figure 1 shows for 773 K the molar volume $V(c)$ and $\alpha = (\partial V/\partial T)_p/V$. The values for pure liquid Ba were calculated from data measured by Hiemstra *et al.*[8] The surface tension Γ was calculated from the bubble pressure difference of two capillaries with diameters of 3.182 and 2.215 mm, respectively. The temperature ranges were almost the same as given in Table 1. $\Gamma$and $(\partial\Gamma/\partial T)_p$ are plotted in Figure 2.

The compressibility was calculated from the velocity of sound which was measured interferometrically at 4 MHz using the pulse-echo

Table 1 Density data of liquid Li/Ba alloys.

Composition (at % Ba)	Liquidus-temp. T_L (K)	Density $\rho(T_L)$ (g/cm^3)	$-(\partial\rho/\partial T)_p * 10^4$ (g/cm^3/K)	Temperature range (K)
0	453	0.514 ± 0.003	1.1 ± 0.07	500-920
5.0	438	0.913 ± 0.004	1.45 ± 0.2	700-910
5.1	438	0.898 ± 0.004	1.80 ± 0.3	710-910
8.8	439	1.241 ± 0.006	1.95 ± 0.3	720-910
13.9	424	1.490 ± 0.007	2.05 ± 0.3	750-940
18.0	428	1.726 ± 0.008	1.65 ± 0.3	720-890
23.4	445	1.922 ± 0.009	1.75 ± 0.3	780-930
31.0	476	2.11 ± 0.010	2.4 ± 0.4	660-830
34.0	491	2.38 ± 0.012	2.1 ± 0.4	740-940
48.2	595	2.72 ± 0.013	3.2 ± 0.4	730-960
52.0	631	2.74 ± 0.014	2.2 ± 0.4	730-950
64.4	745	2.88 ± 0.014	2.3 ± 0.4	830-990
72.5	821	2.98 ± 0.015	2.9 ± 0.4	870-990
80.0	879	3.08 ± 0.016	2.6 ± 0.4	920-1021
100[8]	983	3.345 ± 0.002	2.99 ± 0.21	1003-1103

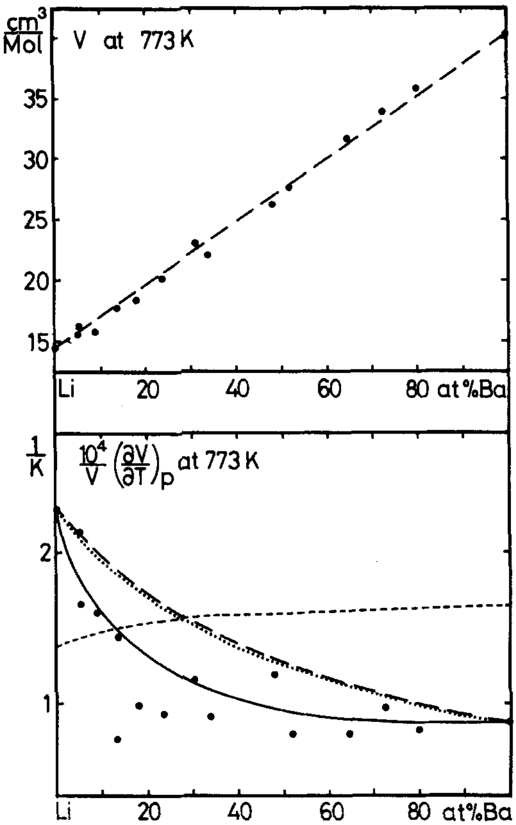

Figure 1 Upper part: Molar volume V of liquid Li/Ba alloys at 773 K. Points: Experimental values. Dashed curve: Calculated from the athermal ($\omega = 0$) FH Eq. (1). Lower part: $(\partial V/\partial T)_p/V$ at 773 K. Points (full drawn line): Experimental values. — —: From FH Eq. (1), ($\omega = 0$). ····: From HS Eq. (2), fitting according to HS1. - - - -: From HS Eq. (2), fitting according to HS2.

technique[7]. The temperature ranges were the same as in Table 1. χ_s and $(\partial \chi_s/\partial T)_p$ are given in Figure 3. The values for liquid Ba were taken from McAlister *et al.*[9] A DSC (Perkin Elmer II) was used to measure the heat capacity C_p with the alloys encapsuled in small containers made from stainless steel. The data points are given in Figure 4 with C_p of pure Ba taken from a compilation of Barin and Knacke[10].

The ordinate scales of the different figures have been chosen such that the scattering of the experimental points becomes clearly visible. The solid lines are drawn to guide the eyes.

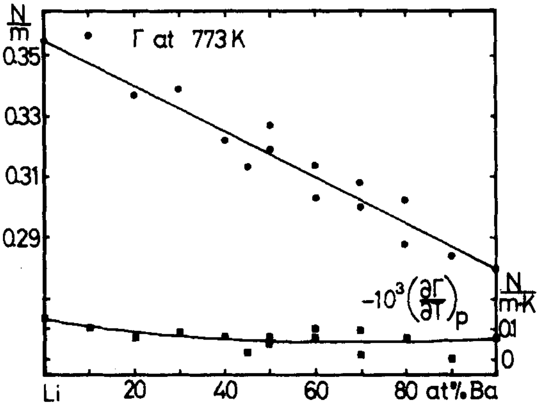

Figure 2 Surface tension Γ (points) and $(\partial\Gamma/\partial T)_p$ (squares) of liquid Li/Ba alloys at 773 K.

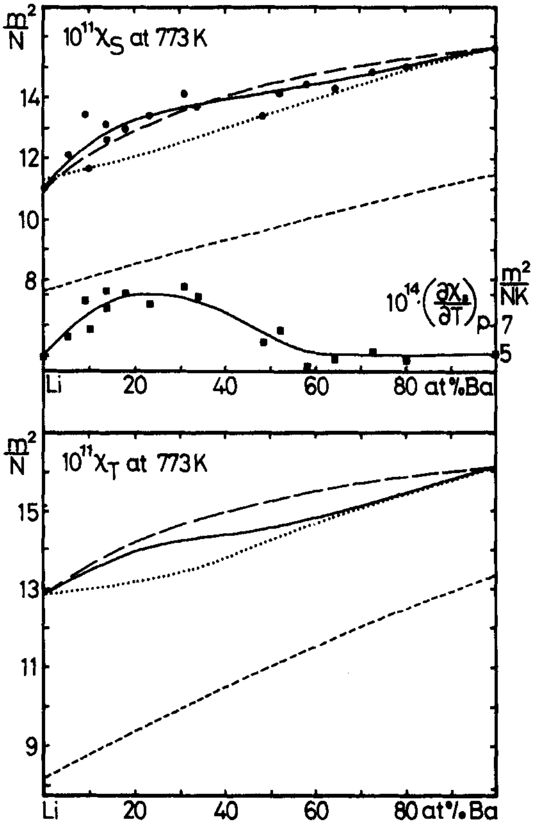

Figure 3 Upper part: Adiabatic compressibility χ_S of liquid Li/Ba alloys at 773 K. Points (full drawn line): Experimental values. --: From FH Eq. (1), ($\omega = 0$). ···: From HS1 formalism. ----: From HS2 formalism. Squares (full drawn line): $(\partial\chi_S/\partial T)_p$. Lower part: Isothermal compressibilities χ_T corresponding to the upper part of the figure.

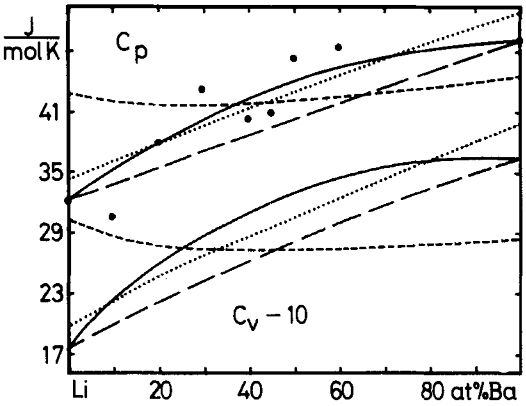

Figure 4 Specific heat of liquid Li/Ba alloys. C_p and C_v plots versus composition are given. The C_v curves are shifted by -10 Jmole^{-1} K^{-1} and are below the corresponding C_p curves. Points: Experimental C_p values. ——: Experimental curves. --: From FH Eq. (1), ($\omega = 0$). ···: From HS1 formalism. ----: From HS2 formalism.

3 DISCUSSION

3.1 Pure Components

The Carnahan Starling equation[2] allows to calculate σ and η of the pure components from ρ_0 and χ_T, the latter was obtained from χ_S, ρ_0, α and C_p. The results are given in Table 2 together with σ_i^n calculated from the corresponding structure factors[1]. The agreement is quite poor which can also be seen by comparing the χ_T values with χ_T^n calculated from σ_i^n and η_i^n. Liquid Li and Ba are just more compressible than the corresponding HS systems. Taking u_g, the uniform background potential, into account does not change much as can be seen by comparing in Table 2 χ_T^{n,u_g} with χ_T^n or σ^{u_g} and η^{u_g} with σ and η, respectively.

Table 2 Compressibility, HS diameter, and packing fraction data of pure liquid Li and Ba.

	T (K)	χ_T	χ_T^n (10^{11} m^2/N)	χ_T^{n,u_g}	σ	σ^n (Å)	σ^{u_g}	η	η^n	η^{u_g}
Li	453	10.38	6.66	6.78	2.673	2.766	2.638	0.446	0.494	0.429
Ba	983	17.49	12.91	13.73	3.811	3.911	3.808	0.425	0.459	0.424

3.2 Alloys

From all our measurements we have the impression that the liquidus temperature of the Li/Ba system is better given by the phase diagram of Keller *et al.*[5] than by the one published by Haase[6].

A quite remarkable result of our studies is the observation of an almost linear variation of the molar volume V with composition c. One could have expected a volume contraction due to the small Li atoms filling up the gaps between the larger Ba spheres. But, indeed, no such effect was found by Lemaignan[11] who studied V of binary steel-ball mixtures and observed linear $V(c)$ curves up to a size difference corresponding approximately to the Li/Ba case. Also $V = (\partial G/\partial p)_T$, calculated from the athermal ($\omega = 0$) FH equation, which is given as a long-dashed curve in Figure 1 is seen to be close to linear. Which means that for Li/Ba Φ_i corresponds to the real volume fraction. It has been shown by Neale and Cusack[12] that in this case $RT(c_1 \ln \Phi_1 + c_2 \ln \Phi_2)$ of the FH Eq. (1) is identical to $-T(\Delta S_{\mathrm{gas}} + S_c)$ of the HS Eq. 2. If the σ_i are assumed to be independent from composition than Eq. (4) yields η linear in volume fraction:

$$\eta = \eta_1^0 + (\eta_2^0 - \eta_1^0)\Phi_2 \tag{5}$$

whereas the same η, if plotted against c, has a positive deviation from linear of up to 3%.

We will now try to find a basis of "ideal" curves which if compared with the experimental results should allow to detect special chemical —or electronical—interactions. Starting points are the athermal FH equation which as we saw corresponds in the present case to a simplified HS equation, and the Mansoori HS Eq. (2). We observed that the above mentioned electronic term ΔE does not help for better understanding the experimental results. Its discussion will be postponed until results for all three systems, Li/Ca, Sr, Ba, are available. However, we take into account the variation with temperature of the HS parameter η and σ, and Eq. (5) is used, if necessary, to calculate the derivatives of ΔF and ΔG corresponding to the different properties investigated[2]. We give in the following figures three "ideal" curves. Long dashed lines, labelled "FH" were obtained from the athermal FH equation and are only based on the following properties of the pure components: V_i and derivatives of V_i, and $C_{p,i}$. Dotted lines "HS1" were obtained by inserting for η_i and σ_i the values calculated from χ_T of the pure components and by fitting $(\partial\eta/\partial T)_v$ to obtain the experimental $(\partial V/\partial T)_p/V$ values of the pure components. HS2 (short dashed lines), finally, is obtained from the corresponding data derived from the structure factors[1].

The FH and HS1 curves of $\alpha = (\partial V/\partial T)_p/V$ given in Figure 1 should be identical because they start from the same α_i of the pure components and for both it was assumed that $V(c)$ remains linear on varying T. The curves are indeed almost indistinguishable, but they are not linear. The experimental $\alpha(c)$ is bent into the same direction, its curvature however is much stronger. Deviations are most pronounced for Li-rich alloys and it is seen that on increasing T, $V(c)$ will get negative excess values. HS2 yields α too small for pure Li and much too large for Ba, only the order of magnitude is correct. HS1 and HS2 yield slightly curved lines $\chi_S(c)$ and $\chi_T(c)$ which are plotted in Figure 3, whereas a s-shaped $\chi_S(c)$ curves resulted from the experiment. On the Ba side $\chi_S(c)$ and $\chi_T(c)$ are well described by HS1. For alloys rich in Li, χ_T is in between the HS1 and FH curves whereas χ_S is even somewhat larger than FH. In this composition range the experimental $(\partial \chi_S/\partial T)_p$ shows most pronounced deviation from linear. Inserting the electronic ΔE term into the HS equations made the results much worse.

FH yields almost straight lines for $C_p(c)$ and $C_V(c)$. The same do the HS plots if η and σ are assumed to be temperature independent. C_V being equal to $\frac{3}{2}R$ in this case. The values obtained from HS1 including $(\partial \eta/\partial T)_v$ terms are not so bad, they only differ by about 10% from the experimental points. But, as is pointed out by Shimoji[2] higher order derivatives of η with respect to T have to be taken into account, already for obtaining meaningful results for C_V of pure liquids. We found no explanation for the positive deviation of the experimental C_p from Neumann Kopp's rule even not by considering the electronic ΔE term.

We know no simple model to calculate the surface tension of a HS mixture. The experimental values given in Figure 2 are just linear in composition.

4 CONCLUSIONS

The strong differences between the experimental points and the HS2 curves demonstrate that Eq. (2), if based on HS parameter deduced from structure data, is a poor starting point to describe α, χ and C of liquid Li/Ba alloys. Inspection of Table 2 shows that the reason for this failure is probably already the bad description of the corresponding properties of the pure components and not so much a wrong description of the behaviour on mixing. This impression is supported by the relatively satisfactory HS1 curves which have been calculated with HS parameter fitted to thermodynamic properties of the pure components. It seems not possible to decide whether HS1 or FH gives a better description of the mixing behaviour, where in the present case FH corresponds to the HS Eq. (2) neglecting the ΔS_η and S_σ terms.

From the composition dependence of α, of χ_S and of $(\partial\chi_S/\partial T)_p$ one has the impression of a somewhat anomalous behaviour on the Li side of the diagrams which is supported by the discussion of the structure data. Remarkably are the strictly linear variations of V with c and the positive deviation of the heat capacity from linear. The latter is said to be typical for systems with tendency for compound formation (Bergman and Komarek[13]). The diffraction pattern of Li/Ba alloys, however, indicate a tendency for segregation[1].

Acknowledgement

We are indebted to Deutsche Forschungsgemeinschaft for financial support.

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