Reports

Raoult's Law and the Melting Point Depression in Mesoscopic Systems

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Data on the melting point depression in small indium or gold particles and in liquid water held between lipid bilayers indicate that these systems obey Raoult's law, with the surface atoms or molecules acting like solute particles in a dilute solution.

MESOSCOPIC SYSTEMS SUCH AS submicrometer-sized metal particles and water molecules held between lipid bilayers show a pronounced melting point depression with decreasing particle size. Moreover, as the size of the particles decreases, the number of particles that can be located at the surface increases. Because atoms or molecules at the surface have physical properties different from those in the volume, it might be possible to view such systems as pseudo-binary solutions. We used Raoult's law of the melting point depression in dilute solutions to investigate this melting point depression in some mesoscopic systems. An intriguing agreement was found between the results obtained from this empirical model and the experimental data. This intuitive application of Raoult's law constitutes an interesting alternative to the thermodynamical approach of Couchman and Jesser (*1*). It is an empirical relation that can be easily checked whenever the melting points of small particles are depressed.

We know that the melting point T_m of ice is depressed in the presence of salt. In general, this phenomenon is observed in dilute solutions. The temperature shift ΔT_m is described by Raoult's law

$$\Delta T_m = -\frac{R T_m^2}{L}\frac{n_1}{n_0} \qquad (1)$$

where R is the gas constant, L is the melting enthalpy, and n_1/n_0 is the molar ratio of solute to solvent, assuming $n_0 >> n_1$. We show here that the melting point depression observed in mesoscopic systems of atoms or molecules can be explained in terms of the melting point of a dilute solution.

Mesoscopic systems are ensembles that have properties between those of single atoms or molecules and those of bulk material in the submicrometer range. In consequence of their properties, mesoscopic systems are of current interest in microelectronics, materials research, and biophysics (*2–4*).

In mesoscopic systems the number of atoms or molecules located at the surface approaches the number in the volume. More than half of them are surface atoms or molecules, if the ratio of the system radius r to the interatomic distance a becomes less than 6, as follows from

$$4\pi r^2 a = 1/2(4\pi/3)r^3$$

where the surface layer equals half the total volume.

Atoms or molecules at the surface have different physical properties from atoms or molecules in the bulk. Only surface atoms or molecules experience a net attractive potential. In a microemulsion, for instance, the molecules at the surfaces are less mobile than those in the water droplets. This effect is due to the stronger water-surfactant interaction at the surface as compared with the water-water interaction in the volume (*5*). This two-component behavior holds for other mesoscopic systems as well. Thus we may apply Raoult's law for dilute solutions in order to understand the observed melting point depression in such pseudo-binary mesoscopic systems. We know of no a priori theoretical reason why surface atoms must shift T_m by the same amount as solute molecules that obey Raoult's law. We show examples in different mesoscopic systems where they do so, within experimental accuracy.

Figures 1 and 2 show data on gold and indium particles, respectively. The T_m values calculated according to Raoult's law are in good agreement with the experimental results. The values for the metal particles follow from Eq. 1 according to the relations

$$n_0 \sim 4\pi/3(r - a)^3$$

and

$$n_1 \sim 4\pi/3[r^3 - (r - a)^3] \qquad (2)$$

Values deduced from a size-dependent thermodynamic theory (*1*) are displayed for comparison.

Figure 3 shows experimental T_m data of interbilayer water (indicated by vertical bars) for three n_1/n_0 values (*6*). Here the surface is imposed by the lipid bilayer distance (*7*). Like the metal particles, the interbilayer water is also well described by Raoult's law of dilute solutions (solid line). In systems with low interbilayer water concentrations, a quasi-continuous melting is observed over a wide temperature range (*6*), as indicated by the broad melting temperature interval in Fig. 3. This behavior was recently predicted for a quasi-molten phase of small particles (*8*).

It is not surprising that T_m shifts by an amount proportional to $1/r$. Such effects are known from Kelvin's equation for the vapor pressure over small droplets (*9*). The surprising result is that the proportionality factor agrees with that predicted by the application of Raoult's law. Whether that

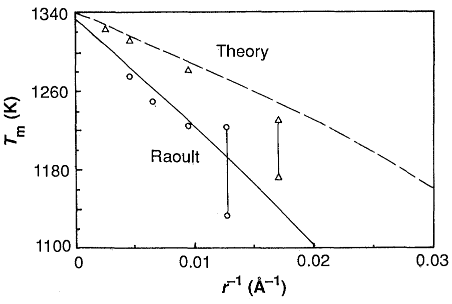

Fig. 1. Melting temperature versus the reciprocal of the particle radius for gold: (——) Raoult (T_m = 1337 K, L = 12,800 J/mol, a = 0.3 nm); (– – –) calculated (*1*); (△ and ○) experimental values after Sambles (*10*) and Buffat and Borel (*11*), respectively, with error bars given for the small size regime.

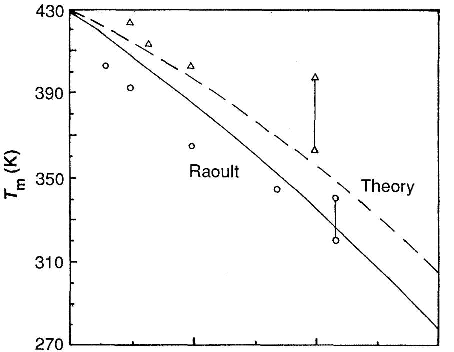

Fig. 2. Melting temperature versus the reciprocal of the particle radius for indium (the interatomar distance, a = 0.3 nm, is calculated from the bulk density; thus there are no free parameters in these fits): (——) Raoult (T_m = 430 K, L = 3270 J/mol, a = 0.3 nm); (– – –) calculated (*1*); (△ and ○) experimental values after Pócza *et al.* (*12*) and Berman and Curzon (*13*), respectively. Error bars as in Fig. 1.

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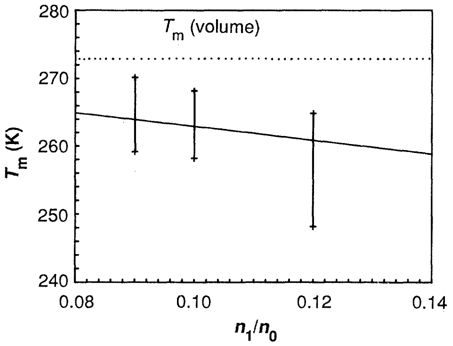

Fig. 3. Melting temperature versus molar ratio for water held between dipalmitoyl phosphatidyl choline bilayers (*6, 7*); the vertical bars indicate quasicontinuous melting over a wide T_m range; (——) Raoult (T_m = 273.15 K, see dotted line, L = 6019 J/mol).

agreement is accidental remains to be seen; we hope that our results will encourage future tests. Certainly, our use of Raoult's law for surface effects is not universally valid. Second-order phase transitions shift their critical temperatures by an amount proportional to $r^{-1/\nu}$ with a correlation length exponent ν that is different from unity. And for small liquid droplets in equilibrium with their vapor, Kelvin's law gives an increase of vapor pressure (proportional to the surface tension), whereas Raoult's law would predict a decrease of vapor pressure (proportional to the vapor pressure).

Our results suggest that certain mesoscopic systems represent binary solutions rather than a single-component material. The two components consist of atoms or molecules placed at the surface and those in the volume, respectively, and they have different physical characteristics. Raoult's law of dilute solutions can be used to describe the observed melting point depression in mesoscopic systems of gold or indium particles and of water held between lipid bilayers. This finding reveals the rivalry between surface and volume with decreasing size of the particles. We regard our observation as a suggestion for further checks in this direction.

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