Diffusion and Viscous Flow in Ideal Binary Liquid Mixtures

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We discuss the dependence of the diffusion coefficient and of the viscosity on the temperature and on the composition for ideal binary liquid mixtures, in particular for the system chlorobenzene + bromobenzene. The activation energy for diffusion is independent of the composition and exceeds the activation energy for viscous flow which is a linear function of the mole fractions.

For most binary liquid systems the dependence of the diffusion coefficient (interdiffusion coefficient) D and of the viscosity η on the thermodynamic temperature T is given by

$$D = B \exp\{-A/RT\}, \quad (1)$$

$$\eta = C \exp\{E/RT\}. \quad (2)$$

Here R is the gas constant while A, B, C, E denote positive empirical parameters which, for constant pressure, are functions of the composition only. The quantity A or E is called the "activation energy" for diffusion or viscous flow, respectively.

We now consider an *ideal* binary liquid mixture, in particular the system chlorobenzene + bromobenzene which has been investigated recently. Denoting the mole fractions of component 1 (chlorobenzene) and of component 2 (bromobenzene) by x_1 and x_2, we conclude from the experimental data [1-3] that the Eqs. (1) and (2) apply and that the additional relations

$$B = B_1 x_1 + B_2 x_2, \quad A = \text{const}, \quad (3)$$

$$C = C_1^{x_1} C_2^{x_2}, \quad E = E_1 x_1 + E_2 x_2 \quad (4)$$

hold where B_1, B_2, C_1, C_2, E_1, E_2 are positive constants. The quantity E_1 or E_2 is the activation energy for viscous flow of the pure liquid component 1 or 2, respectively. (The viscosities of the pure components and the two limiting values of the diffusion coefficient follow from the equations above with $x_1 = 1$ and $x_2 = 1$.)

Comparing and contrasting the relations (3) with the relations (4), we notice that the composition dependence of the viscosity is more complex than that of the diffusion coefficient. In particular, the activation energy for diffusion (A) is independent of the composition while the activation energy for viscous flow (E) is a linear function of the mole fractions. This is true, at least, for the ideal liquid system chlorobenzene + bromobenzene.

Using all the available data [1, 3] for diffusion in the system chlorobenzene + bromobenzene (temperature range: 10 °C to 40 °C) and fitting the adjustable constants in Eqs. (1) and (3), we find:

$$B_1 = 152.2 \cdot 10^{-5}\ \text{cm}^2\,\text{s}^{-1},$$

$$B_2 = 118.9 \cdot 10^{-5}\ \text{cm}^2\,\text{s}^{-1},$$

$$A = 11.24 \cdot 10^3\ \text{J mol}^{-1}.$$

The values of C_1, C_2, E_1, E_2 for the same system (temperature range of viscosity measurements: 0 °C to 80 °C) have been listed earlier [2].

The constants B_1 and B_2 are not comparable to C_1 and C_2. But A may be compared with E_1 and E_2:

$$E_1 = 8.88 \cdot 10^3\ \text{J mol}^{-1}, \quad E_2 = 9.38 \cdot 10^3\ \text{J mol}^{-1}.$$

We conclude that A exceeds E_1 or E_2 and thus exceeds any value of E [see Equation (4)]. This seems to be a general rule [1].

Hence, even for an ideal mixture, there is no simple relation between diffusion (interdiffusion) and viscous flow.

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