

Viscosity of Binary Mixtures

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The viscosities of the mixtures $\text{CCl}_4\text{--CHCl}_3$, $\text{C}_6\text{H}_6\text{--CH}_2(\text{C}_6\text{H}_5)_2$ and $\text{C}_7\text{H}_{16}\text{--C}_{16}\text{H}_{34}$ have been measured in an ordinary Ostwald viscometer. The deviation from linearity in the fluidity is positive in the first case, negative in the last two. The first case is discussed using the theorem of corresponding states, and it is shown that the dipole interaction is responsible for the asymmetry in the "excess fluidity".

In recent years the theory of liquid mixtures has reached a high degree of perfection. Using the average potential model of Prigogine and coworkers¹ one can predict, at least semi-quantitatively, the thermodynamic functions for mixtures when one knows the properties of the pure components.

With regard to a property like the viscosity of mixtures the situation is less satisfactory. The only workable theory of which we are aware is that of Eyring and coworkers² and its extensions by Grunberg³. This theory, however, contains an empirical correction term of appreciable magnitude, and in our opinion it can therefore primarily be considered as a convenient way of classifying experimental results.

The difficulty in setting up a theory for viscosity of mixtures is that one does not have a good theory for viscosity of pure liquids. A more promising way of attacking the problem for the time being is therefore to make a semi-phenomenological theory in which one uses the properties of the pure liquids without trying to account for them by means of a molecular model. The natural vehicle for such work is the theory of corresponding states, since the fluidity of a liquid can be described using only two parameters, *viz.* $\Phi = A \exp(-E/RT)$.

Such a development was suggested by K. Meyer⁴ as early as 1909, but it was not until the idea of an average potential in liquid mixtures had been developed that it actually became possible.

The method we use has been developed by Thomaes⁵ and used successfully on the mixture $\text{CCl}_4\text{--C}(\text{CH}_3)_4$. In order to test the method further we have measured the viscosity of a mixture where dipolar effects are predominant, namely $\text{CCl}_4\text{--CHCl}_3$ and two mixtures for which size effects dominate, namely $\text{C}_6\text{H}_6\text{--CH}_2(\text{C}_6\text{H}_5)_2$ and $\text{C}_7\text{H}_{16}\text{--C}_{16}\text{H}_{34}$. The ordinary thermodynamic properties of these mixtures are well known, and the surface tensions of the mixtures have recently been measured in this laboratory⁶.

EXPERIMENTAL

The liquids were purified as described by Koefoed and Villadsen⁶. The viscosities were measured in an ordinary Ostwald viscometer which in each case was standardized on one of the pure liquids. The values for the viscosity of the pure liquids (CCl_4 , C_6H_6 and C_7H_{16}) were taken from the book by Timmermans⁷. Table I gives the results obtained for the fluidity and its deviation from the linearly interpolated fluidity.

Table I.

1. CCl_4 — CHCl_3 . (X is the mole-fraction of CHCl_3). $T = 25.01^\circ\text{C}$.

X	Φ cp^{-1}	$\Phi - \Phi_{\text{lin}}$ cp^{-1}
0.000	1.103	0.000
0.151	1.226	0.011
0.328	1.367	0.020
0.610	1.580	0.024
0.803	1.716	0.017
1.000	1.845	0.000

2. C_6H_6 — $\text{CH}_2(\text{C}_6\text{H}_5)_2$. (X is mole-fraction of diphenylmethane.) $T = 29.70^\circ\text{C}$.

X	Φ cp^{-1}	$\Phi - \Phi_{\text{lin}}$ cp^{-1}
0.000	1.773	0.000
0.113	1.364	-0.253
0.204	1.140	-0.350
0.238	0.975	-0.398
0.523	0.666	-0.382
0.686	0.534	-0.285
0.801	0.469	-0.192
0.893	0.427	-0.106
1.000	0.383	0.000

3. C_7H_{16} — $\text{C}_{16}\text{H}_{34}$. (X is mole-fraction of $\text{C}_{16}\text{H}_{34}$.)

X	Φ cp^{-1}	$\Phi - \Phi_{\text{lin}}$ cp^{-1}	Φ cp^{-1}	$\Phi - \Phi_{\text{lin}}$ cp^{-1}
	$T = 20.02^\circ\text{C}$	$T = 20.02^\circ\text{C}$	$T = 30.00^\circ\text{C}$	$T = 30.00^\circ\text{C}$
0.000	2.445	0.000	2.747	0.000
0.097	1.808	-0.429	2.062	-0.455
0.195	1.370	-0.655	1.582	-0.705
0.492	0.678	-0.707	0.811	-0.767
0.785	0.385	-0.371	0.481	-0.404
1.000	0.291	0.000	0.370	0.000

It should perhaps be remarked that in the last two cases, for which the "excess fluidity" is negative, the "excess viscosity" is positive, as it is also in the case of CCl_4 — CHCl_3 .

THEORY

We want to treat the fluidity of mixtures by the method of corresponding states, *i.e.*, we want to get a dimensionless fluidity by multiplying it with a suitable combination of the molecular mass and the parameters which charac-

terize the intermolecular potential, ε and r . The dimension of fluidity is $\text{g}^{-1} \text{cm sec}$, and it is therefore reduced by multiplication with $(m\varepsilon)^{1/2} r^{-2}$. We shall neglect the pressure dependence of the viscosity, so that we can assume that two liquids at the same reduced temperature are at corresponding states as long as we only consider their viscosity.

For a mixture, ideal with respect to fluidity ², we have

$$\Phi = X_1\Phi_{11} + X_2\Phi_{22}$$

where Φ_{11} and Φ_{22} are the fluidities of the pure components, and X_1 and X_2 are the mole-fractions. For a non-ideal solution we therefore set

$$\Phi = X_1\Phi_1 + X_2\Phi_2$$

where Φ_1 and Φ_2 are quantities to be determined.

Formally we have:

$$\Phi_{11}(T_1) = \frac{r_{11}^2}{(m_{11}\varepsilon_{11})^{1/2}} \tilde{\Phi}(T_1)$$

$$\Phi_1(T) = \frac{r_1^2}{(m_1\varepsilon_1)^{1/2}} \tilde{\Phi}(T)$$

where $\tilde{\Phi}(T)$ denotes a reduced fluidity at the (non-reduced) temperature T , T_1 is an undetermined temperature, and T is the temperature of the mixture. Assuming that $m_1 = m_{11}$, that is, assuming that the effective mass of species 1 in the flow process is independent of the mole-fraction we have

$$\Phi_1(T) = \Phi_{11}(T_1) \left(\frac{\varepsilon_{11}}{\varepsilon_1} \right)^{1/2} \left(\frac{r_1}{r_{11}} \right)^2 \frac{\tilde{\Phi}(T)}{\tilde{\Phi}(T_1)}$$

If in this expression we choose $\tilde{T}_1 = \tilde{T}$, *i.e.*, $T_1 = T \frac{\varepsilon_{11}}{\varepsilon_1}$ the two reduced fluidities cancel, and we therefore can express $\Phi_1(T)$ in terms of the pure compound at another temperature:

$$\Phi_1(T) = \Phi_{11} \left(T \frac{\varepsilon_{11}}{\varepsilon_1} \right) \left(\frac{\varepsilon_{11}}{\varepsilon_1} \right)^{1/2} \left(\frac{r_1}{r_{11}} \right)^2$$

An analogous expression is found for Φ_2 .

The quantities ε_1 and r_1 which we have introduced in this way are assumed to be "average potentials" and "average distances" in the liquid mixture, *i.e.*,

$$\varepsilon_1 = X_1\varepsilon_{11} + X_2\varepsilon_{12}$$

where ε_{11} is the maximum interaction energy between two 1-molecules, and ε_{12} is the maximum interaction energy between a 1-molecule and a 2-molecule. Analogous expressions are used for r_1 , ε_2 and r_2 . For r_{12} we take, as long as dipolar effects can be neglected $r_{12} = \frac{1}{2}(r_{11} + r_{22})$, and for ε_{12} we take, when no other information can be obtained,

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}$$

For the mixture $\text{CCl}_4\text{—CHCl}_3$ we have, when dipolar effects are neglected, $\epsilon_{11} = \epsilon_{22}$, $r_{11} \neq r_{22}$, but $|r_{11} - r_{22}| \ll r_{11} + r_{22}$. We shall therefore first investigate this case where the only differences which can cause non-ideal behaviour is a difference in size.

We set $2 \frac{r_{22} - r_{11}}{r_{11} + r_{22}} = \rho$ and have

$$\begin{aligned}\Phi_1 &= \Phi_{11}(1 - \rho X_2) \\ \Phi_2 &= \Phi_{22}(1 + \rho X_1)\end{aligned}$$

neglecting higher powers of ρ . Therefore

$$\Phi = X_1\Phi_1 + X_2\Phi_2 = X_1\Phi_{11} + X_2\Phi_{22} + (\Phi_{11} - \Phi_{22})\rho X_1X_2$$

The deviation from linearity is positive when $\Phi_{11} - \Phi_{22}$ has the same sign as ρ , which is the most common thing. Its maximum value is $\frac{1}{4}\rho(\Phi_{11} - \Phi_{22})$. For the mixture we consider $r_{11} = 6.62 \text{ \AA}$ and $r_{22} = 6.10 \text{ \AA}$, so that $\rho = -0.082$. The maximum deviation is then 0.015 cp^{-1} .

It is known, however, that for $\text{CCl}_4\text{—CHCl}_3$ dipolar effects are predominant. From the measurements of McGlashan, Prue and Sainsbury⁸ and Cheesman and Whitaker⁹ one finds, for $X_1 = X_2 = \frac{1}{2}$, $h^E/g^E = 2.14$, where h^E stands for the excess molar enthalpy of mixing and g^E for the excess molar Gibbs function of mixing, and this almost satisfies the relation of Pople¹⁰, $g^E = Ts^E = \frac{1}{2}h^E$, valid for mixtures where dipolar effects are predominant and differences in polarizability between the two species can be neglected.

To treat the dipolar effects we set

$$\begin{aligned}\epsilon_{ij} &= \epsilon_{ij}^0(1 + \psi_{ij}) \\ r_{ij} &= r_{ij}^0(1 + \varphi_{ij})\end{aligned}$$

and

where ψ_{ij} and φ_{ij} are small perturbations which stem from the dipole interaction. For details on this method, we refer to chapter 14 in the book by Prigogine¹.

Using the technique described there, we find

$$\begin{aligned}\psi_{11} &= \psi_1 = \varphi_{11} = \varphi_1 = 0 \\ \psi_{22} &= \frac{2}{3}\Gamma & \varphi_{22} &= -\frac{1}{18}\Gamma \\ \psi_2 &= \frac{2}{3}X_2(1 + 3\rho X_1)\Gamma \\ \varphi_2 &= \frac{1}{18}X_2(1 + 3\rho X_1)\Gamma\end{aligned}$$

with $\Gamma = \frac{\mu_2^4}{r_{22}^6 \epsilon_{22} kT}$ where μ_2 is the dipole moment of CHCl_3 .

Therefore we have

$$\begin{aligned}\Phi_1 &= \Phi_{11} \left(\frac{r_1}{r_{11}} \right)^2 \\ \Phi_2 &= \Phi_{22} \left(T + \frac{2}{3} \vartheta T \right) \left(\frac{r_2}{r_{22}} \right)^2 \left(1 + \frac{1}{3} \vartheta \right)\end{aligned}$$

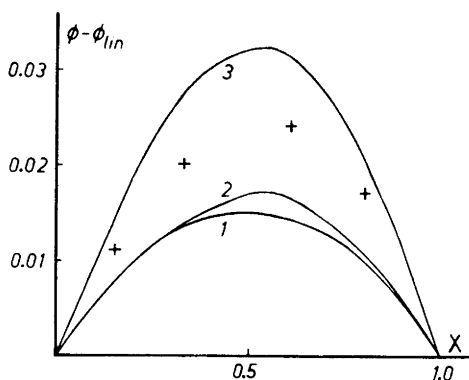


Fig. 1. Excess fluidity in reciprocal centipoise for the system $\text{CCl}_4\text{-CHCl}_3$. 1 size effect, 2 dipolar effect, 3 sum of 1 and 2, + experimental points.

with $\vartheta = (1 - X_2 + 3\rho X_1 X_2)I$; $I = 0.013$ at 25°C . Here we have again neglected higher powers of ρ and ϑ , and we shall therefore also expand Φ_{22} in a Taylor series from T retaining only the linear term. We then have

$$\begin{aligned}\Phi_2 &= \Phi_{22}(T) \left(\frac{r_2}{r_{22}}\right)^2 \left[1 + \vartheta \left(\frac{2}{3} \frac{T\Phi'_{22}}{\Phi_{22}} + \frac{4}{9}\right)\right] \\ &= \Phi_{22} \left(\frac{r_2}{r_{22}}\right)^2 (1 + 2.47 \vartheta)\end{aligned}$$

at 25°C , using data from the book by Timmermans⁷. Substituting this into the expression for Φ we have $\Phi = \Phi_{lin} + 0.061 X_1 X_2 + 0.059 X_2(1 - X_2 + 0.25 X_1 X_2)$

Within this approximation we see that the size effect and the dipolar effect simply add. Fig. 1 shows the experimental values of $\Phi - \Phi_{lin}$ and the curves for the size effect, the dipole effect and the sum of the two. Although the curve for the sum overshoots the mark considerably, it is seen that qualitatively it has all the right features including the asymmetry.

For the other two mixtures we have not so far been able to give a satisfactory theoretical development along these lines, but we hope to return to this problem in a later publication.

We are indebted to Dr. G. Thomaes for valuable discussions and for letting us see his paper before its publication.

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Received May 14, 1958.