

Thermodynamics of Oligomeric Alkane Liquid Mixtures at High Pressures

BY ERIC DICKINSON

Procter Department of Food Science, University of Leeds, Leeds LS2 9JT

Received 16th February, 1982

For binary liquid mixtures of n-alkanes, the previously reported changes in sign and magnitude of the experimental excess volume with increasing pressure are found to be consistent with the phenomenological theory of corresponding states.

In describing the thermodynamic state of a liquid mixture of volume V at pressure p and temperature T , we say that the applied pressure is high if it is comparable to or greater than the 'internal pressure' $T(\partial p/\partial T)_V$. Typically, $T(\partial p/\partial T)_V$ takes a value of *ca.* 2 kbar, and therefore experiments done at atmospheric pressure (*ca.* 1 bar) occur at effectively negligible external pressure. As recognized by Bridgman,¹ experimental behaviour at low or negligible pressure is a poor guide to what is likely to happen at high pressure.

For binary liquid mixtures of n-alkanes at ambient pressure, the reported excess volumes are invariably negative.² The magnitude of the volume change increases with (a) the temperature and (b) the difference in chain length of the pure-component molecules. This behaviour can be understood in terms of the principle of corresponding states as applied to mixtures of oligomers by Prigogine.³ With oligomers belonging to the same homologous series, the negative sign of the excess volume is the direct consequence of the form of the reduced equation of state, and the magnitude of the excess volume is related in a simple way to the difference in the reduced temperatures of the pure components.⁴ Positive volume changes are observed experimentally at atmospheric pressure,² but only with mixtures of oligomers that are chemically different. In non-polar examples of this latter type (*e.g.* n-alkane + linear dimethylsiloxane), the positive excess volume is attributed⁵ to the unequal pressure reduction factors of the two components.

In a recent experimental study of several binary mixtures of n-alkanes at pressures up to 5 kbar, Dymond *et al.*^{6,7} found that the magnitude of the excess volume decreases with increasing applied pressure. Most interestingly, however, they report that the excess volume eventually becomes positive so long as the temperature and pressure are high enough. It is the purpose of this short paper to examine whether these new high-pressure data are consistent with the corresponding-states theory for mixtures of homologues. We shall not be concerned here with any anomalies that arise from proximity to critical points.

According to the phenomenological formulation of the principle of corresponding states,⁸ the reduced volume \tilde{V}_i of a pure oligomeric liquid i of molar volume $V_{m,i}$ is a universal function of the reduced temperature $\tilde{T}_i = T/T_i^*$ and reduced pressure $\tilde{p}_i = p/p_i^*$:

$$\tilde{V}_i = V_{m,i}/V_i^* = \tilde{V}_i(\tilde{p}_i, \tilde{T}_i). \quad (1)$$

The reduction factors V_i^* , T_i^* and p_i^* for a given homologous series depend only on the chain length n . For a mixture of molar volume V_m , eqn (1) may be rewritten as

$$\tilde{V} = V_m / \langle V^* \rangle = \tilde{V}(\langle \tilde{p} \rangle, \langle \tilde{T} \rangle) \quad (2)$$

where $\langle \tilde{T} \rangle = T / \langle T^* \rangle$ is the reduced temperature of the mixture, $\langle \tilde{p} \rangle = p / \langle p^* \rangle$ is the reduced pressure of the mixture, and $\langle V^* \rangle$, $\langle T^* \rangle$ and $\langle p^* \rangle$ are average volume, temperature and pressure reduction factors, respectively.

The molar excess volume V_m^E of a binary mixture ($i = 1, 2$) at constant temperature and pressure is given by

$$V_m^E = (x_1 V_1^* + x_2 V_2^*) \tilde{V}(\langle \tilde{p} \rangle, \langle \tilde{T} \rangle) - x_1 V_1^* \tilde{V}(\tilde{p}_1, \tilde{T}_1) - x_2 V_2^* \tilde{V}(\tilde{p}_2, \tilde{T}_2) \quad (3)$$

where x_1 is the mole fraction of component 1. The magnitude of the predicted excess volume depends to a considerable extent on the rules for calculating $\langle \tilde{p} \rangle$ and $\langle \tilde{T} \rangle$ from the pure-component reduced pressures and temperatures. For a mixture of chain molecules having uniform force fields and no special 'end effects', Patterson and coworkers^{9,10} have argued that the reduced quantities for the mixture are given by

$$\langle \tilde{p} \rangle^{-1} = \phi_1 \tilde{p}_1^{-1} + \phi_2 \tilde{p}_2^{-1} \quad (4)$$

$$\langle \tilde{T} \rangle = X_1 \tilde{T}_1 + X_2 \tilde{T}_2. \quad (5)$$

The volume fraction ϕ_1 in eqn (4) and the surface fraction X_1 in eqn (5) are defined by

$$\phi_1 = x_1 V_1^* / (x_1 V_1^* + x_2 V_2^*) \quad (6)$$

$$X_1 = x_1 p_1^* V_1^* / (x_1 p_1^* V_1^* + x_2 p_2^* V_2^*). \quad (7)$$

The two fractions are equal if $p_1^* = p_2^*$.

For conceptual purposes, it is convenient to regard the excess volume as being a sum of three contributions:

$$V_m^E = V_m^E(\text{I}) + V_m^E(\text{II}) + V_m^E(\text{III}). \quad (8)$$

The quantity $V_m^E(\text{I})$ is the notional contribution to V_m^E from mixing the components at constant reduced pressure; $V_m^E(\text{II})$ is the contribution from mixing at constant reduced temperature; and $V_m^E(\text{III})$ is a cross-term. When the pure-component reduced temperatures are not too dissimilar, we may expand $\tilde{V}(\langle \tilde{p} \rangle, \tilde{T}_1)$ and $\tilde{V}(\langle \tilde{p} \rangle, \tilde{T}_2)$ about $\tilde{V}(\langle \tilde{p} \rangle, \langle \tilde{T} \rangle)$ in powers of $\Delta \tilde{T} = \tilde{T}_1 - \tilde{T}_2$. To second order in $\Delta \tilde{T}$, $V_m^E(\text{I})$ then has the form

$$V_m^E(\text{I}) = -(x_1 X_2 V_1^* - x_2 X_1 V_2^*) \Delta \tilde{T} (\partial \tilde{V} / \partial \langle \tilde{T} \rangle)_{\langle \tilde{p} \rangle} \\ - \frac{1}{2} (x_1 X_2^2 V_1^* + x_2 X_1^2 V_2^*) (\Delta \tilde{T})^2 (\partial^2 \tilde{V} / \partial \langle \tilde{T} \rangle^2)_{\langle \tilde{p} \rangle}. \quad (9)$$

At atmospheric pressure, when mixing occurs at essentially constant reduced pressure, $V_m^E(\text{I})$ is the only contribution that need be considered.⁵ At high pressures, when \tilde{p}_1^{-1} and \tilde{p}_2^{-1} are not too dissimilar, it is convenient, because of the form of eqn (4), to expand $\tilde{V}(\tilde{p}_1, \langle \tilde{T} \rangle)$ and $\tilde{V}(\tilde{p}_2, \langle \tilde{T} \rangle)$ about $\tilde{V}(\langle \tilde{p} \rangle, \langle \tilde{T} \rangle)$ in powers of $\Delta(\tilde{p}^{-1}) = \tilde{p}_1^{-1} - \tilde{p}_2^{-1}$. To second order in $\Delta(\tilde{p}^{-1})$ we have

$$V_m^E(\text{II}) = -\frac{1}{2} (x_1 \phi_2^2 V_1^* + x_2 \phi_1^2 V_2^*) [\Delta(\tilde{p}^{-1})]^2 (\partial^2 \tilde{V} / \partial \langle \tilde{p}^{-1} \rangle^2)_{\langle \tilde{T} \rangle}. \quad (10)$$

We note that the expansion in $\Delta(\tilde{p}^{-1})$ is not valid at low pressure. At high pressure, the final term $V_m^E(\text{III})$ in eqn (8) involves the product of $\Delta \tilde{T} [\Delta(\tilde{p}^{-1})]$ and the cross-derivative $(\partial^2 \tilde{V} / \partial \langle \tilde{T} \rangle \partial \langle \tilde{p}^{-1} \rangle)$.

It is clear from eqn (8)-(10) that a detailed knowledge of the reference equation of state is needed for the calculation of excess volumes at finite reduced pressures, and

that the scarcity of precise pure-component equation-of-state data is the main limitation on quantitative prediction. We prefer to concentrate here on qualitative and semi-quantitative aspects. Of particular interest is the simple expression for V_m^E obtained if $p_1^* = p_2^*$:

$$V_m^E = -\frac{1}{2}(x_1\phi_2^2V_1^* + x_2\phi_1^2V_2^*)(\Delta\tilde{T})^2(\partial^2\tilde{V}/\partial\langle\tilde{T}\rangle^2)_{\langle\tilde{p}\rangle} + \mathcal{O}[(\Delta\tilde{T})^3]. \quad (11)$$

This assumption of equal pressure reduction factors has been shown⁴ to be valid for a mixture of two n-alkanes. According to eqn (11), the sign and magnitude of V_m^E are determined by the sign and magnitude of $(\partial^2\tilde{V}/\partial\langle\tilde{T}\rangle^2)_{\langle\tilde{p}\rangle}$, which in turn depend on the curvature of V as a function of T for the conformal reference fluid at constant pressure. It is well known that, at low pressures, the isobaric expansivity $\alpha_p = (1/V)(\partial V/\partial T)_p$ of a pure liquid increases as the temperature rises $[(\partial^2 V/\partial T^2)_p > 0]$ and ultimately diverges at the gas-liquid critical point. What is less widely known is that at high pressures the sign of $(\partial^2 V/\partial T^2)_p$ is reversed. According to Bridgman,¹ the first trace of this phenomenon was seen by Amagat¹¹ near the upper end of his pressure range (*ca.* 3 kbar), but apparently the effect seemed to Amagat so unlikely that he ascribed it to experimental error! With measurements up to higher pressures, Bridgman and many others have conclusively demonstrated the reality of the effect. Recalling the thermodynamic identity involving the heat capacity C_p

$$(\partial C_p/\partial p)_T = -T(\partial^2 V/\partial T^2)_p \quad (12)$$

Bridgman notes¹ that 'this reversal in the sign of $(\partial^2 V/\partial T^2)_p$ is obviously a most important point for any theory of liquids'.

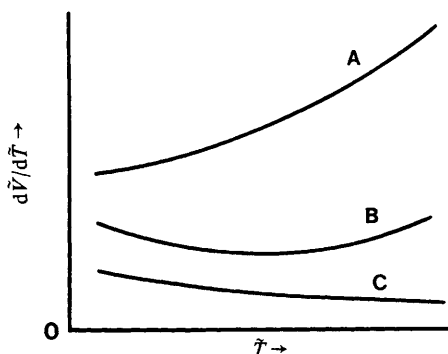


FIG. 1.—Variation in the derivative of reduced volume \tilde{V} with respect to reduced temperature \tilde{T} . The quantity $d\tilde{V}/d\tilde{T}$ is plotted against \tilde{T} for three fixed and widely separated values of the reduced pressure: (A) low reduced pressure ($p \sim 0$), (B) intermediate reduced pressure [$p \sim T(\partial p/\partial T)_V$], (C) extremely high reduced pressure [$p \gg T(\partial p/\partial T)_V$].

In fig. 1 the form of $(\partial\tilde{V}/\partial\tilde{T})_{\tilde{p}}$ as a function of \tilde{T} for a real liquid is shown schematically for low, intermediate and high reduced pressures. At low reduced pressures $(\partial\tilde{V}/\partial\tilde{T})_{\tilde{p}}$ is an increasing function of \tilde{T} , and so V_m^E from eqn (11) is negative at all temperatures. On the other hand, at extremely high reduced pressures $(\partial\tilde{V}/\partial\tilde{T})_{\tilde{p}}$ is a slow, monotonically decreasing function of \tilde{T} , and V_m^E from eqn (11) is small and positive at all temperatures. At intermediate reduced pressures (well away from the critical point), the predicted excess volume is small in magnitude, and its sign may be positive or negative depending on whether $(\partial\tilde{V}/\partial\tilde{T})_{\tilde{p}}$ is a decreasing or increasing function of \tilde{T} . That is, at intermediate pressures, the corresponding-states theory predicts that V_m^E is negative at high temperatures and positive at low temperatures.

To get an idea of the pressure at which the predicted excess volume changes sign, let us consider the system n-hexane(1)+n-hexadecane(2). It is convenient to choose n-undecane as the conformal reference substance because its chain length [$n = \frac{1}{2}(6+16)$] is such that the reduced temperature of the reference substance is almost exactly equal to that of the equimolar mixture ($\phi_1 \approx 0.29$). The second derivative ($d^2\tilde{V}/d\tilde{T}^2$) at constant pressure is related to the expansivity α_p by

$$(d\alpha_p/dT) + \alpha_p^2 = \alpha'_p = (\tilde{V}T^{*2})^{-1}(d^2\tilde{V}/d\tilde{T}^2). \quad (13)$$

Based on specific-volume data¹² for n-undecane in the temperature range 303–573 K and the pressure range 0–5 kbar, fig. 2 shows a plot of α'_p against pressure at 373 K. The same graph shows experimental values of V_m^E for an equimolar mixture of n-hexane + n-hexadecane at 373 K over the same pressure range.⁶ The strong correlation between the sign and relative magnitude of V_m^E and the sign and relative magnitude of α'_p confirms the semi-quantitative validity of eqn (11) for n-alkane mixtures.

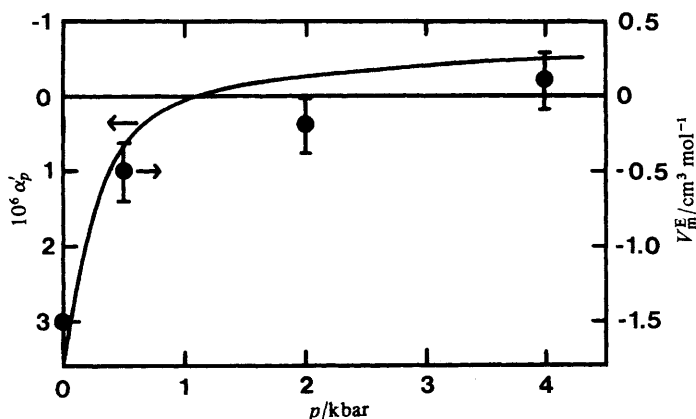


FIG. 2.—Correlation between the function α'_p [defined in eqn (13)] for n-undecane [ref. (12)] and the equimolar excess volume V_m^E for n-hexane + n-hexadecane [ref. (6)]. The quantities α'_p and V_m^E at 373 K are plotted against the pressure p .

As a final comment on eqn (11), we note that when $(\partial^2\tilde{V}/\partial\langle\tilde{T}\rangle^2)_{\langle\tilde{p}\rangle}$ is small in magnitude it may change in sign across the composition range. This is because $\langle\tilde{T}\rangle$ is itself a function of composition [eqn (5)]; and it could so happen that $(\partial^2\tilde{V}/\partial\langle\tilde{T}\rangle^2)_{\langle\tilde{p}\rangle}$ is negative at low values of x_1 and positive at high values of x_1 . For n-hexane + n-hexadecane at intermediate pressures, this would imply a predicted negative excess volume at high mole fractions of n-hexane and a positive one at low mole fractions. Indeed, such S-shaped V_m^E against x_1 curves are found⁶ experimentally at 3 ± 1 kbar.

¹ P. W. Bridgman, *The Physics of High Pressures* (Bell and Sons, London, 1949), chap. 5.

² Y. P. Handa and G. C. Benson, *Fluid Phase Equilibria*, 1979, **3**, 185.

³ I. Prigogine, *The Molecular Theory of Solutions* (North-Holland, Amsterdam, 1957), chap. 16.

⁴ D. Patterson and J. M. Bardin, *Trans. Faraday Soc.*, 1970, **66**, 321.

⁵ E. Dickinson and I. A. McLure, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 2328.

⁶ J. H. Dymond, K. J. Young and J. D. Isdale, *J. Chem. Thermodyn.*, 1979, **11**, 887.

⁷ J. H. Dymond, J. Robertson and J. D. Isdale, *J. Chem. Thermodyn.*, 1982, **14**, 51.

⁸ J. Hijmans, *Physica*, 1961, **27**, 433.

⁹ S. N. Bhattacharyya, D. Patterson and T. Somecynsky, *Physica*, 1964, **30**, 1276.

¹⁰ D. Patterson and G. Delmas, *Trans. Faraday Soc.*, 1969, **65**, 708.

¹¹ E. H. Amagat, *Ann. Chim. Phys.*, 1893, **29**, 68.

¹² A. K. Doolittle, *J. Chem. Eng. Data*, 1964, **9**, 275.