

GAS-LIQUID CRITICAL TEMPERATURES OF n-ALKANE+n-ALKANE AND CYCLOALKANE+n-ALKANE MIXTURES

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The prediction of the properties of mixtures containing n-alkanes is of great interest in the petroleum industry and consequently the critical properties of n-alkane+n-alkane mixtures have been investigated by many workers. Previously we used the segment concept to correlate the critical temperatures of n-alkane+n-alkane mixtures using only the pure n-alkane critical temperatures.¹ We have also compared the critical temperatures of a range of quasi-spherical molecule mixtures with those predicted from the van der Waals theory.²⁻⁴ There are several reasons for expecting that the agreement between the van der Waals treatment and experiment will be poor⁴ for mixtures containing n-alkanes. The component molecules are not, in general, even approximately spherical and the molecules do not obey the same principal of corresponding states.⁵ However, in this paper it is shown that agreement is surprisingly good.

Theory

Elsewhere^{2-4,6} it has been shown that for the van der Waals one-fluid model the critical temperature of a mixture T_m^c is given by

$$T_m^c = T_x^c \left(1 + \frac{x_1 x_2}{16} \left(\frac{3}{T_x^c} \times \frac{\partial T_x^c}{\partial x_2} + \frac{1}{V_x^c} \times \frac{\partial V_x^c}{\partial x_2} \right)^2 \frac{(x_1 + r x_2)^2}{x_1 + r^2 x_2} \right) \quad (1)$$

where

$$T_x^c V_x^c = x_1^2 T_{11}^c V_{11}^c + x_2^2 T_{22}^c V_{22}^c + 2x_1 x_2 T_{12}^c V_{12}^c \quad (2)$$

$$V_x^c = x_1^2 V_{11}^c + x_2^2 V_{22}^c + 2x_1 x_2 V_{12}^c \quad (3)$$

and r is the size ratio. T_{ij}^c and V_{ij}^c are the pseudo-critical parameters characterizing the interaction between i and j molecules. The approximations in the derivation of these equations have been discussed elsewhere.^{2-4,6}

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¹ Hicks, C. P., and Young, C. L., *Trans. Faraday Soc.*, 1970, **66**, 1340.

² Hicks, C. P., and Young, C. L., *Trans. Faraday Soc.*, 1971, **67**, 1598.

³ Hicks, C. P., and Young, C. L., *Trans. Faraday Soc.*, 1971, **67**, 1605.

⁴ Hicks, C. P., and Young, C. L., *J. chem. Thermodynamics*, in press.

⁵ McGlashan, M. L., and Potter, D. J. B., *Proc. R. Soc. (A)*, 1962, **276**, 478.

⁶ Leland, T. W., Rowlinson, J. S., and Sather, G. A., *Trans. Faraday Soc.*, 1968, **64**, 1447.

To compare theory and experiment it is necessary to use combining rules to evaluate the critical parameters characterizing the interaction between unlike molecules. In the present paper we have used the Lorentz-Berthelot rules

$$T_{12}^c = (T_{11}^c T_{22}^c)^{1/2} \quad (4a)$$

$$V_{12}^c = \frac{1}{8}(\sqrt[3]{V_{11}^c} + \sqrt[3]{V_{22}^c})^3 \quad (4b)$$

and we have used the ratio of molar volumes at 293 K to estimate r^1 . Values of the standard deviation between predicted and experimental critical temperatures for the n-pentane+n-alkane mixtures are as follows (values in K): C₆, 0.6; C₇, 2.1; C₈, 2.5; C₉, 2.2; C₁₀, 3.3; C₁₁, 2.9; C₁₂, 4.2; C₁₃, 5.0. The data were taken from the references given in ref.¹

The agreement between theory and experiment is good except for mixtures in which the size differences are very large. This is true of the n-alkane and n-alkane+cycloalkane data in general.

Secondly we have fitted the experimental data to the equimolar composition critical temperature using the general combining rule⁶ equation (5) instead of the Berthelot rule:

$$T_{12}^c = \xi(T_{11}^c T_{22}^c)^{1/2} \quad (5)$$

where ξ is an adjustable parameter. The values of ξ for the various systems are given in Table 1. There is no simple trend of ξ for mixtures of a given molecule with

TABLE 1

COMPARISON OF ξ OBTAINED FROM THE EXPERIMENTAL DATA AT EQUIMOLAR COMPOSITION WITH THOSE PREDICTED BY THE HUDSON AND MCCOUBREY COMBINING RULE

Mixture	Exptl	Calc.	Mixture	Exptl	Calc.	Mixture	Exptl	Calc.
n-Alkane + n-Alkane Mixtures						Cyclopentane + n-Alkane Mixtures		
C ₂ +C ₃	1.009	0.992	nC ₅ +nC ₆	1.000	0.997	cC ₅ +nC ₅	1.004	0.997
+nC ₄	0.990	0.975	+nC ₇	0.997	0.991	+nC ₆	0.998	0.989
+nC ₅	0.988	0.954	+nC ₈	0.986	0.983	+nC ₇	0.993	0.978
+nC ₇	0.892	0.908	+nC ₉	1.006	0.974	+nC ₈	0.989	0.966
C ₃ +nC ₄	1.000	0.995	+nC ₁₀	1.012	0.964	+nC ₉	0.984	0.954
+nC ₅	0.982	0.984	+nC ₁₁	1.014	0.954	Cyclohexane + n-Alkane Mixtures		
+nC ₆	0.988	0.969	+nC ₁₂	0.989	0.944	cC ₆ +C ₂	0.953	0.954
+nC ₇	0.968	0.951	+nC ₁₃	0.964	0.934	+nC ₅	1.016	1.000
+nC ₈	0.963	0.934	nC ₆ +nC ₇	1.001	0.998	+nC ₆	1.003	0.997
nC ₄ +nC ₅	0.999	0.997	+nC ₈	1.002	0.993	+nC ₇	0.999	0.990
+nC ₆	1.002	0.988	nC ₇ +nC ₈	1.001	0.999	+nC ₈	0.997	0.982
+nC ₇	1.002	0.977				+nC ₉	0.991	0.973
+nC ₈	1.003	0.965						

a second component of increasing chain-length. In the case of molecules of very similar size the value is very nearly unity. For the cycloalkane mixtures and ethane mixtures the values of ξ decreases with the increasing size differences. The values of ξ for the propane+n-alkane, n-butane+n-alkane, and n-pentane+n-alkane mixtures appear to increase, go through a maximum, and then decrease again as the n-alkane chain

increases. These values are only fitted to the critical temperature at equimole fraction and values of ξ chosen to give the best fit over the composition range are generally slightly smaller. Similar trends are observed but the maximum is not so pronounced. Values of ξ may be predicted by more elaborate combining rules than equation (4) such as the Hudson and McCoubrey rule⁷ (equation (6)):

$$\xi = \frac{2(I_1 I_2)^{1/2}}{I_1 + I_2} \times \frac{2^6 V_{11}^c V_{22}^c}{(\sqrt[3]{V_{11}^c} + \sqrt[3]{V_{22}^c})^6} \quad (6)$$

where I is the ionization potential. However, for the n-alkane+n-alkane mixtures the Berthelot rule (equation (4)) is often in better agreement with experiment than the more complex rule. Similar behaviour has been observed by Knobler *et al.*⁸ for the mixed second virial coefficients of n-alkane mixtures. However, for propane+n-heptane and propane+n-octane both the mixed second virial coefficient^{5,9} and the critical temperatures give ξ values in reasonable agreement with the Hudson and McCoubrey rule.

It is possible to introduce shape factors into the van der Waals treatment¹⁰ but at the present in the authors' opinion too little is known about these factors for their inclusion to add very much of value. Obviously the shape of a molecule does have a marked effect on the critical properties of pure substances. For example, the critical compressibility, Z^c , of the n-alkane is less than that of the corresponding cycloalkane^{11,12} whereas Z^c would be constant if the substances obeyed the same principle of corresponding states. However, it is almost certain that for mixtures the shape of the molecules is relatively less important in critical properties than in the thermodynamic properties of mixtures at room temperatures.

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⁹ Cruickshank, A. J. B., Windsor, M. L., and Young, C. L., *Trans. Faraday Soc.*, 1966, **62**, 2341.

¹⁰ Leland, T. W., Rowlinson, J. S., Sather, G. A., and Watson, I. D., *Trans. Faraday Soc.*, 1969, **65**, 2034.

¹¹ Kudchadker, A. P., Alani, G. H., and Zwolinski, B. J., *Chem. Rev.*, 1968, **67**, 659.

¹² Young, C. L., *Trans. Faraday Soc.*, in press.