

EXCESS ENTROPY OF THE SYSTEMS OF MOLECULES DIFFERING IN SIZE AND SHAPE

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Received September 24th, 1981

The excess entropy of mixing of mixtures of hard spheres and spherocylinders is determined from an equation of state of hard convex bodies. The obtained dependence of excess entropy on composition was used to find the accuracy of determining ΔS^E from relations employed for the correlation and prediction of vapour-liquid equilibrium. Simple rules were proposed for establishing the mean parameter of nonsphericity for mixtures of hard bodies of different shapes allowing to describe the P-V-T behaviour of solutions in terms of the equation of state for pure substance. The determination of ΔS^E by means of these rules is discussed.

From the results of the statistical-thermodynamic study of fluids¹ follows that the liquid structure is given above all by the intermolecular repulsive forces. With regard to their character (steep increase with decreasing distance), the structure of real systems can be determined from the relations describing the behaviour of model systems of hard, generally nonspherical bodies corresponding, as to the shape and size, to the structure of molecules of systems studied.

The excess entropy of mixing of real solutions, which reflects the changes in structure on forming a mixture of a given composition from pure components, consequently, can be estimated very well from the relations for ΔS^E of model systems of hard particles; these expressions can easily be determined from equations of state for one- and multicomponent systems.

Recently, two variants of equation of state of hard convex bodies²⁻⁴ have been proposed in our laboratory. On comparing with pseudoexperimental data for one- and multicomponent systems of hard convex bodies, it has been found^{5,6} that the proposed equations yield the description of P-V-T behaviour within the limits of errors of pseudoexperimental determinations. These two equations of state along with the formerly proposed more general, slightly less accurate modified scaled particle theory (MSPT) relation have been used to determine ΔS^E ; the curves obtained can be considered as exact results which can serve to verify the validity of relations for determining a so-called configuration entropy in semiempirical expressions for estimating ΔG^E or activity coefficients in solutions.

Unlike the equations of state of pure substances, where the compressibility factor depends only on the parameter of nonsphericity and packing fraction, the compressibility factor of mixture is dependent on several variables. This fact can be a certain problem when using it in semiempirical relations. Therefore, in the second part of this work, the rules are studied for determining the mean parameter of nonsphericity of mixture on the basis of the values for individual components of solutions.

THEORETICAL

In the following study, three equations of state are considered:

a) The equation derived by the author² in the framework of the scaled particle theory,

$$\frac{PV}{RT} = \frac{1}{1-y} + \frac{3\alpha y}{(1-y)^2} + \frac{\alpha^2 y^2 (3-y)}{(1-y)^3}, \quad (1a)$$

where P is the pressure, V the volume, R the gas constant, T the absolute temperature, y the packing fraction, $y = \varrho V_i$, ϱ is the particle density, $\alpha = R_i S_i / 3V_i$ is the parameter of nonsphericity, V_i is the volume S_i the surface and R_i the mean curvature integral divided by 4π , of a particle of the given type i .

For a mixture of hard particles of types i, j, \dots with geometric quantities $R_i, S_i, V_i, R_j, S_j, V_j, \dots$, holds

$$\frac{PV}{RT} = \frac{1}{1-v} + \frac{rs}{\varrho(1-v)^2} + \frac{qs^2(3-v)}{9\varrho(1-v)^3}, \quad (1b)$$

where $r = \varrho \sum x_i R_i$, $q = \varrho \sum x_i R_i^2$, $s = \varrho \sum x_i S_i$ and $v = \varrho \sum x_i V_i$; x_i is the mole fraction of component i .

The MSPT equation of state is quite general, holds both for the convex bodies and linear fused hard sphere bodies. Its accuracy decreases with increasing parameter α and packing fraction; for the spherocylinders with $\alpha = 1.2$ (considered henceforth in this work) at $y = 0.45$ it is, however, still possible to find full agreement with pseudoexperiment.

b) Nezbeda³ has proposed, on the basis of the analysis of pseudoexperimental data on the compressibility factors of hard spherocylinders with various ratios of length to width, the equation

$$\frac{PV}{RT} = \frac{1}{1-y} + \frac{3\alpha y}{(1-y)^2} + \frac{(\alpha^2 + 4\alpha - 2)y^2 - \alpha(5\alpha - 4)y^3}{(1-y)^3}, \quad (2a)$$

which was extended to mixtures by Pavlíček and coworkers⁴

$$\frac{PV}{RT} = \frac{1}{1-v} + \frac{rs}{\varrho(1-v)^2} + \frac{3qs^2 - 2r^2s^2/\varrho + 12r^2st/\varrho - 18rstw/\varrho + (12t - 5s)qsv}{9\varrho(1-v)^3}, \quad (2b)$$

where $t = \varrho \sum x_i V_i / R_i$ and $w = \varrho \sum x_i V_i / S_i$.

Recently the author of this work has obtained, from the study of virial coefficients of hard convex bodies⁷, the relation

$$\frac{PV}{RT} = \frac{1}{1-y} + \frac{3xy}{(1-y)^2} + \frac{3x^2y^2(1-2y) + 5xy^3}{(1-y)^3} \quad (3a)$$

and the corresponding relation for solutions

$$\frac{PV}{RT} = \frac{1}{1-v} + \frac{rs}{\varrho(1-v)^2} + \frac{qs^2(1-2v) + 5rsv^2}{3\varrho(1-v)^3}. \quad (3b)$$

On comparing with the pseudoexperimental data for hard spherocylinders of different ratios of length to width and with the data for the binary system hard spheres – hard spherocylinders, it was found that the equations of state (2) and (3) describe accurately (within experimental errors) the behaviour of the given systems in the entire region of liquid densities and values of parameter of nonsphericity.

For the difference of entropy of the given system and an ideal gas under the same conditions holds

$$(S - S^*)/R = - \int_0^{\varrho} \varrho^{-1} (PV/RT - 1) d\varrho; \quad (4)$$

considering further that all the three equations of state can be written in one general form

$$\frac{PV}{RT} = \frac{1}{1-y} + \frac{D_2y}{(1-y)^2} + \frac{D_3y^2 + D_4y^3}{(1-y)^3}, \quad (5)$$

we can express the excess entropy of mixing as follows

$$\begin{aligned} \frac{S^E}{R} = & \sum_i x_i \left\{ \ln \frac{V_s}{V_i} + \left[A_i \ln(1-y_i) - A_s \ln(1-v) \right] + \right. \\ & \left. + \left[B_i \frac{y_i}{(1-y_i)} - B_s \frac{v}{(1-v)} \right] + \left[C_i \frac{y_i}{(1-y_i)^2} - C_s \frac{v}{(1-v)^2} \right] \right\}. \quad (6) \end{aligned}$$

The coefficients $A_i - C_i$ and $A_s - C_s$ for Eq. (1) take the form

$$\begin{aligned} A_i &= \alpha_i^2 - 1, & B_i &= 3\alpha_i, & C_i &= \alpha_i^2, \\ A_s &= (qs^2/9qv^2 - 1), & B_s &= rs/qv, & C_s &= qs^2/9qv^2; \end{aligned} \quad (7)$$

in case of the equation of state (2) holds

$$\begin{aligned} A_i &= 5\alpha_i^2 - 4\alpha_i - 1, & B_i &= 7\alpha_i^2 - 5\alpha_i + 1, & C_i &= -2\alpha_i^2 + 4\alpha_i - 1, \\ A_s &= (5qs^2/9qv^2 - 4qst/3qv^2 - 1), \\ B_s &= (9qrsv + 6qqs^2 + r^2s^2 - 6r^2st + 9rstw - 18qqs^2)/9qv^2, \\ C_s &= (-qqs^2 - r^2s^2 + 6r^2st - 9rstw + 6qqs^2)/9qv^2. \end{aligned} \quad (8)$$

In a similar way one can obtain from the equation of state (3)

$$\begin{aligned} A_i &= 6\alpha_i^2 - 5\alpha_i - 1, & B_i &= (15\alpha_i^2 - 9\alpha_i)/2, & C_i &= (-3\alpha_i^2 + 5\alpha_i)/2, \\ A_s &= (2qs^2/3qv^2 - 5rs/3qv - 1), \\ B_s &= (5qs^2/6qv^2 - 3rs/2qv), \\ C_s &= (-qs^2/6qv^2 + 5rs/6qv). \end{aligned} \quad (9)$$

The dependence of excess entropy on composition, determined from Eq. (6) with the parameters given by Eqs (7)–(9), is illustrated in Fig. 1. The computation was carried out for the hard spheres – spherocylinders ($\gamma = 2$) model system at constant packing fraction $y_i = v = 0.45$. It follows from Fig. 1 that the curves calculated from relations (7) and (9) are practically undistinguishable whereas the curve, corresponding to values of Eq. (8) (*i.e.* to the Nezbeda equation and its extension (2b)), are always higher; the difference corresponds to the uncertainty of the ΔS^E determination. In the same figure, also the dependence of ΔS^E is depicted as calculated from the Flory–Huggins relation⁸

$$\Delta S^E/R = \sum_i x_i \ln (V_i/\sum x_i V_i), \quad (10)$$

(where the symbol V_i denotes the molar volume of component i), which probably describes best, from several quasi-lattice relations, the effect of size and/or shape on the value of ΔS^E . It is evident from Fig. 1 that the results corresponding to Eq. (10) acquire only about half the values which can be considered as exact. It is therefore possible to say that the Flory–Huggins relation – and more generally, the expressions derived in the framework of the quasi-lattice theories (*e.g.*, from the configuration

contribution in the expression for activity coefficient in the UNIFAC method⁹ follows the value of $\Delta S^E/R = 0.061$ at $x_1 = 0.5$ in comparison with $\Delta S_{F-H}^E/R = 0.10$ and the correct value $\Delta S^E/R = 0.19-0.20$) considerably underestimate the effect of size and shape of molecules on the structure, and consequently, on ΔS^E of solutions.

In semiempirical approaches, the molecule shape and size are usually characterized by the volume V_i and parameter of nonsphericity α_i whereas the geometric quantities S_i and R_i are not known. Then V_i and α_i suffice to characterize the P-V-T behaviour of pure substance, but do not allow to describe the behaviour of a mixture of more components characterized in this way. In this case the knowledge is desirable of a rule for calculating the mean parameter of nonsphericity, $\bar{\alpha}$, on the basis of α_i values of single components.

The simplest rule, used recently by Kreglewski and Chen¹⁰ when applying their equation of state to vapour-liquid equilibrium of solutions at higher pressures can be written as

$$\bar{\alpha} = \sum x_i \alpha_i \quad (11)$$

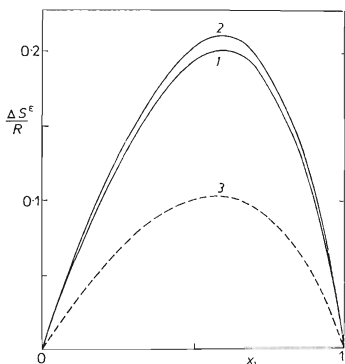


FIG. 1

Excess entropy of mixing as a function of composition. 1 The curve calculated from Eq. (6) and equations of state (1) and (3), 2 the curve calculated from Eq. (2), 3 the curve calculated from Eq. (10)

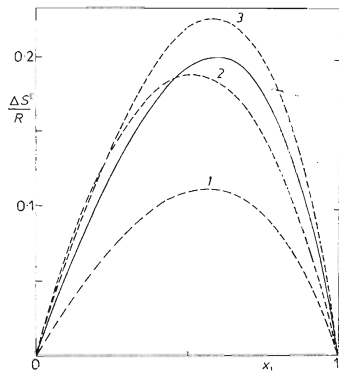


FIG. 2

Comparison of dependences of excess entropy of mixing determined from Eqs (6) and (14) and rules (11)–(13) with exact calculation. 1 Rule (11), 2 Eq. (12), 3 Eq. (13), — exact dependence

The next rule is of entirely empirical character,

$$\bar{\alpha} = (\sum x_i \alpha_i^{-3})^{-1/3}. \quad (12)$$

Theoretical basis is involved in the rule expressed by Eq. (13)

$$\bar{\alpha} = \sum x_i (\alpha_i V_i)^{1/3} \sum x_i (\alpha_i V_i)^{2/3} / \sum x_i V_i, \quad (13)$$

giving in the special case of a mixture of hard spheres of various diameters the exact value of the second term coefficient of equations of state (1b)–(3b).

The knowledge of mean parameter of nonsphericity for a given composition makes it possible to calculate the mixture compressibility factor from the equation of state of pure substance (1a)–(3a) in which we consider $\bar{\alpha}$ instead of α and v instead of y . Eq. (6) holds henceforth for excess entropy of mixing, however, the coefficients $A_s - C_s$ are then functions of parameter $\bar{\alpha}$ only. For instance, in case of Eq. (1) holds

$$\begin{aligned} A_i &= \alpha_i^2 - 1, & B_i &= 3\alpha_i, & C_i &= \alpha_i, \\ A_s &= \bar{\alpha}^2 - 1, & B_s &= 3\bar{\alpha}, & C_s &= \bar{\alpha}. \end{aligned} \quad (14)$$

The courses of dependences of excess entropy of mixing on composition are compared in Fig. 2 for the previously considered system of hard spheres and spherocylinders; the curves were calculated from Eqs (6) and (14) on using rules (11)–(13) for determining $\bar{\alpha}$. The exact dependence, following from relations (6) and (7), is plotted by solid line. It follows from the comparison that the use of rule (11) results in low values of ΔS^E ; the estimate of ΔS^E in terms of rule (12) is substantially better, however, the shape of ΔS^E vs x_1 curve does not correspond to the right course. Probably the best agreement with the exact determination of ΔS^E is yielded on using rule (13). The same conclusions hold also for the application of rules (11)–(13) in combination with Eqs (2) and (3); the agreement in case of Eq. (2) and rule (13) is especially good.

CONCLUSION

From the study of the model system of hard spheres and hard spherocylinders follows that a) the equations of state of hard convex particles proposed in our laboratory (which were shown before to interpret reliably the known pseudoexperimental data) yield the values of excess entropy of mixing which all agree well together and can be used as reference data, b) the relations used in semiempirical expressions to describe the vapour–liquid equilibrium considerably underestimate or completely neglect the effect of mutual size and shape of molecules on ΔS^E , c) the lately proposed

rules for determining the mixture mean parameter of nonsphericity yield substantially better description of the compressibility factor or excess entropy of mixing than those used hitherto. The given rules allow to determine excess entropy from the relation which has a good theoretical basis and satisfies the requirement of simplicity.

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Translated by J. Linek.