HEATS OF MIXING OF NONELECTROLYTES

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The first-order perturbation method is applied to a rapid estimation of heats of mixing of binary liquid mixtures containing molecules with a negligible polarity and approximately spherical symmetry. The calculation is based on the approximate perturbation expansion of the Helmholtz free energy up to first order and requires the knowledge of the radial distribution function of the hard-sphere reference system at the contact point. Generalized relations are used for estimating the molecular parameters. The calculated values are compared with experimental data on six mixtures. Good qualitative agreement was achieved in all cases investigated.

In our earlier paper[1] we have derived a simple relation which enables a relatively accurate prediction of heats of vaporization of pure components formed by nonpolar and approximately spherically symmetrical molecules.

In this work we consider a possibility of using a simple perturbation variant for calculating enthalpic functions of liquid mixtures of nonpolar components. This calculation starts from a simplified statistical-thermodynamics model and requires only the knowledge of commonly available physical constants of pure components such as density and critical data. Commonly employed combination rules are also employed for parameters describing the molecular interaction of different components.

THEORETICAL

First-order perturbation methods[2,3] can also be applied to multicomponent systems. Most often these methods employ properties of the reference system of additive hard spheres, for which it holds $d_{kl} = (d_{kk} + d_{ll})/2$. If a simple square-well potential $u_{kl}(r)$, which depends only on the intermolecular distance r as

$$\begin{aligned} u_{kl}(r) &= +\infty\,, && r \leqq \sigma_{kl}\,, \\ u_{kl}(r) &= -\varepsilon_{kl}\,, \quad \text{for} && \sigma_{kl} < r \leqq \gamma_{kl}\sigma_{kl}\,, \\ u_{kl}(r) &= 0\,, && r > \gamma_{kl}\sigma_{kl}\,, \end{aligned} \tag{1}$$

is used for representing the intermolecular forces acting between particles k and l, the total potential interaction energy W of a system containing s components can be divided into reference, W_0, and perturbation, W^{p}, terms

$$W = \sum_{k,l=1}^{s} \sum_{i<j} u_{kl}(r_{ij}) = W_0 + W^{\mathrm{p}}\,, \tag{2}$$

so that the term W_0 is the energy of the reference mixture of hard spheres with diameters $d_{kl} = \sigma_{kl}$ and the perturbation term includes only attractive forces. The pair perturbation potential is defined through the relations $u_{kl}^{\mathrm{p}}(r) = u_{kl}(r)$ for $r > \sigma_{kl}$, $u_{kl}^{\mathrm{p}}(r) = 0$ for $r \leqq \sigma_{kl}$.

The perturbation contribution to the internal energy, $\Delta U_{\mathrm{m}} = U_{\mathrm{m}} - U_{0\mathrm{m}}$, where $U_{0\mathrm{m}}$ is the internal energy of the reference hard-sphere mixture at the same conditions, can be approximated, after neglecting the higher-order terms, by the following relation[2]

$$\Delta U_{\mathrm{m}} = 2\pi N n \sum_{k,l=1}^{s} x_k x_l \int_0^{\infty} u_{kl}^{\mathrm{p}}(r)\, g_0^{kl}(r)\, r^2\, \mathrm{d}r\,, \tag{3}$$

where x_k are mole fractions of components in the mixture, N is Avogadro's constant, $n = N/V$ is the number density, V is the molar volume of the mixture and $g_0^{kl}(r)$ denotes the radial distribution functions in the mixture of additive hard spheres. In the derivation of this relation we made use of the fact that the hard-sphere diameter does not depend on temperature in our simple perturbation variant.

Similarly as in our preceding paper[1], which had been dealing with the calculation of heats of vaporization of pure components, each of the radial distribution functions was approximated by two linear sections. The slope of the first straight line is determined by the value of $g_0^{kl}(=\sigma_{kl})r = g_{\mathrm{m}}^{kl}$ at the contact point of hard spheres, which depends on the number density $n = N/V$ and composition x_k $(k = 1, \ldots, s - 1)$, and by g_0^{kl} $(r = \lambda_{kl}\sigma_{kl}) = 1$. The quantity λ_{kl} represents an average over a narrow range of intermolecular distances $(r/\sigma_{kl} \in \langle 1{\cdot}20, 1{\cdot}35 \rangle)$, for which it holds $g_0^{kl}(r) = 1$. In agreement with the preceding paper[1], the value of λ_{kl} was set equal to $\lambda_{kl} = \lambda = 1{\cdot}275$. For $r > \lambda\sigma_{kl}$, the reference radial distribution function was approximated by a constant $g_0^{kl}(r > \lambda\sigma_{kl}) = 1$.

For the radial distribution function in the hard-sphere mixture at the contact point, we employed the Carnahan–Starling approximation[4], which describes the behaviour of hard spheres better than expressions derived from the compressibility[5] or virial[6] Percus–Yevick solutions. The approximation used can be expressed in the form

$$g_{\mathrm{m}}^{kl} = g_0^{kl}(d_{kl}) = \frac{1}{1 - \xi_3} + \frac{3 d_{kk} d_{ll}}{2 d_{kl}} \frac{\xi_2^2}{(1 - \xi_3)^2} +$$

$$+ \frac{1}{2}\left(\frac{d_{kk}d_{ll}}{d_{kl}}\right)^2 \frac{\xi_2^2}{(1-\xi_2)^3}\,, \quad \xi_i = \sum_{k=1}^{s} \eta_k d_{kk}^i\,, \tag{4}$$

where $n_k = \frac{1}{6}\pi n_k$, n_k is the number density of component k, $n_k = x_k N/V$, and x_k is its mole fraction. The diameters of hard spheres, d_{kl}, are in our case identical with the parameters σ_{kl} of the potential employed.

By inserting the approximations described into relation (*2*), we obtain the following expression for the perturbation contribution to the Helmholtz free energy of a binary mixture

$$\Delta U_m = -\tfrac{1}{6}\pi N n \sum_{k,l=1}^{2} x_k x_l \varepsilon_{kl} \sigma_{kl}^3 [4\gamma_{kl}^3 + 1{\cdot}973 g_m^{kl}(n, x_k) - 5{\cdot}974]\,, \tag{5}$$

in which the function $g_m^{kl}(n, x_k)$ defined through relation (*4*) depends on the density n and composition x_k (the unit of energy for ΔU_m is determined by the choice of the unit for ε_{kl}, the volume unit of the density $n = N/V$ must be identical with the unit for σ_{kl}).

Since the internal energy of the reference system ($U_0 = 3/2NkT$, k is Boltzmann's constant) is independent of volume, the expression $RT - \Delta U_m$ is the heat of vaporization into an ideal gas state at constant composition and pressure (if the liquid phase volume is neglected in comparison with the vapour phase). Since, at pressures $p < 1$ atm, the vapour phase behaves almost ideally, we can write

$$\Delta H_{vap} = RT - \Delta U_m\,. \tag{6}$$

The same assumptions combined with an analogous expression for ΔU of pure components[1] lead to the following relation for the excess enthalpy ΔH^E

$$\Delta H^E \approx \Delta U^E = \Delta U_m - x_1\,\Delta U_1 - x_2\,\Delta U_2\,, \tag{7}$$

where ΔU_1 and ΔU_2 are the perturbation contributions to the internal energy of pure components. The last three equations can be evaluated only if the molar volume of the mixture is known. In our simple variant, the effect due to the volume change during mixing was neglected.

For a successful application of the variant proposed, the best possible description of the intermolecular interaction through the simple square-well potential is required – an appropriate method must be used for the choice of the parameters ε_{kl}, σ_{kl} and γ_{kl}. Values of ε_{kk} and σ_{kk} were obtained from critical data by generalized estimation relations[7,8]. The method employed for determining the parameter γ_{kk} includes to a certain extent a correction for the realistic course of the intermolecular potential, since the value of γ_{kk} was obtained by comparing the expression for the second virial coefficient in a system of particles obeying the square-well potential with the value of this coefficient for the Lennard-Jones potential[9] with the same parameters ε_{kk} and σ_{kk}, *i.e.*,

$$\gamma_{kk}^3 = (1 - B/b_0 + \Delta)/\Delta\,, \tag{8}$$

where $\Delta = \exp(\varepsilon_{kk}/kT) - 1$, B or b_0 is the second virial coefficient in the real or hard – sphere system, resp.

The parameters ε_{kl}, σ_{kl} and γ_{kl}, which describe the interaction between different molecules, were approximated by the simplest and most often used combination rules[10], which are in accordance with the additivity in the reference hard – sphere system.

$$\begin{aligned} \varepsilon_{kl} &= \sqrt{(\varepsilon_{kk}\varepsilon_{ll})}\,, \\ \sigma_{kl} &= (\sigma_{kk} + \sigma_{ll})/2\,, \\ \gamma_{kl} &= (\gamma_{kk} + \gamma_{ll})/2\,. \end{aligned} \tag{9}$$

RESULTS AND DISCUSSION

Calculated and experimental values of the heat of mixing – ΔH^E_{calc} and ΔH^E_{exp} – in six binary liquid mixtures at different molar ratios are mutually compared in Table I. The choice of the testing mixtures was limited not only by requirements on spherical symmetry and a minimal polarity of their molecules, but also by the possibility of a comparison with experimental data[11]. The temperatures were also selected according to this criterion.

The agreement is worse than in the case of heats of vaporization[1]. However, we must realize that the values of ΔH^E calculated by this variant represent small differances between large numbers. Nevertheless, in comparison with more exact theories[12-14], our results cannot be denoted as unsatisfactory. (A comparable quality between our results and those following from the more exact theories of liquids has been achieved mainly by the fact that our variant uses an experimental value of density, whereas in a complete perturbation solution this value is calculated.) The agreement for the CCl_4–C_7H_8 and CCl_4–CH_2Cl_2 systems can be considered as satisfactory even from a quantitative point of view, in other cases the agreement is only qualitative. Owing to a small absolute value of ΔH^E (approximately by two orders lower than ΔH_{vap}), this simplified method cannot be expected to produce better results.

The fact, that deviations between experimental data and ΔH^E_{calc} are for some mixtures large and positive whereas for others they are negative, indicates that main inaccuracies in our calculation are not due to the approximation used for the radial distribution function (even though the effect of an unequal accuracy in the approximation of its course at different densities manifests itself to a certain extent also here), but that the results are affected by other factors, especially by an insufficient approximation of the intermolecular forces. (This fact can be documented *e.g.* on the behaviour of systems containing $CHCl_3$. Theoretical values possess always a correet sign, but the absolute values are always considerably lower. Results of these calculations are not included in Table I.)

Further, due to low values of ΔH^E, our results are considerably affected by the neglect of the excess volume ΔV^E, because relation (*5*) depends on density and, in contrast to several other theories, this neglect of ΔV^E is not mutually compensated in the resulting expression containing several terms of opposite signs. This effect cannot be specified more quantitatively owing to the lack of suitable experimental data on ΔV^E.

The effect of other approximations is essentially identical with that described and discussed in our preceding work[1].

In the calculation of ΔH^E we must also consider the effect of combination rules employed for parameters ε_{kl}, σ_{kl} and γ_{kl} (relation (*9*)), since these relations are so far to a large extent of an empirical nature. The use of the linear combination rule for σ_{kl} follows readily from the use of the additive hard-sphere system as a reference. The same method as in the case of pure components could be used for determining the parameter γ_{kl} – the description of the cross interaction should be somewhat better with this parameter. However, with respect to other crude approximations, we employed the simpler rule (*9*). Besides that, the analogous method for determining γ_{kk} depends already on combination rules for ε_{kl} and σ_{kl}. If no specific interactions between molecules of different components are assumed, we can expect that the commonly employed geometric mean rule for ε_{kl} will yield a relatively good estimate.

TABLE I

The Comparison between Calculated Heats of Mixing (J . mol^{-1}) and Experimental Data[a]

Mixture	T, K	x_1	ΔH^E_{calc}	ΔH^E_{exp}	δ^b
$SiCl_4$(1)–CCl_4(2)	293·35	0·921	99·90	56·07	0·78
$SiCl_4$(1)–$TiCl_4$(2)	293·35	0·273	197·12	151·88	0·30
$SiCl_4$(1)–C_6H_{12}(2)	293·15	0·550	302·72	251·06	0·41
CCl_4(1)–C_7H_8(2)	303·15	0·330	42·72	36·82	0·16
CCl_4(1)–C_6H_6(2)	288·15	0·430	53·90	95·69	−0·44
CCl_4(1)–CH_2Cl_2(2)	297·85	0·490	638·45	589·94	0·08
Ar(1)–Kr(2)	115·8	0·500	−62[c])	—	—

[a] Values of ΔH^E_{exp} taken from ref.[11]; [b] $\delta = (\Delta H^E_{calc} - \Delta H^E_{exp})/\Delta H^E_{exp}$; [c] Results of calculations from the literature: Monte-Carlo −34 ± 40 (ref.[15]), −29 (ref.[16]), −18 (ref.[17]); the perturbation theory −54 (ref.[13]), −42 (ref.[11]), −10 (ref.[19]); the van der Waals theory −50 (ref.[13]).

To eliminate the uncertainty introduced into our calculations by the approximations used for real molecular interactions (the assumed course of the realistic potential, the use of generalized relations for determining parameters in this potential, the choice of combination rules, *etc.*), we have performed a comparison with pseudoexperimental Monte-Carlo data[15-17] (which correspond with the behaviour of an Ar–Kr system). This comparison is together with the other data given in Table I. The resulting agreement is satisfactory.

We can summarize our results by stating that even though the simplified perturbation variant applied to the calculation of heats of mixing of nonpolar liquids yields a worse agreement than in the case of heats of vaporization[1], the results obtained give a reasonable qualitative agreement. This is a valuable result especially because of the fact that direct calorimetric data at different temperatures and compositions are scarce and, on the other hand, data calculated from vapour–liquid equilibria are obtained rather laboriously and the error corresponding to the computation method employed lies in many cases between ±25 and 30%. Our method of calculation requires only the knowledge of common characteristics of pure components, *i.e.*, density and critical data.

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