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Prediction of excess enthalpies of ketone–alkane systems from infinite dilution activity coefficients

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Abstract

A new approach to predicting excess enthalpies of binary mixtures from infinite dilution activity coefficients is proposed. Owing to the use of infinite dilution activity coefficients, this approach can provide the sole predicted values of excess enthalpies for a considered system at a specific temperature. It has been successfully applied to predicting the excess enthalpies of 23 ketone–alkane systems.

Keywords: Alkane; Binary system; Excess enthalpy; Infinite dilution activity coefficient; Ketone

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List of symbols

(aa)	parameter in MOSCED model
A^E	excess molar Helmholtz energy
$\Delta E_{21}, \Delta E_{12}$	binary parameters as defined by Eq. (7)
G^E	excess molar Gibbs free energy
H^E	excess molar enthalpy
k	Boltzmann constant in Table 1
(NC_H)	number of skeletal carbon atoms for alkane component

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(NC_K)	number of skeletal carbon atoms for ketone component
N_0	Avogadro constant
q_i	molecular surface area parameter of component i
r_i	molecular volume parameter of component i
R	universal gas constant
T	absolute temperature
v_i	saturated liquid volume of component i at 20°C
v_{ji}	volume defined as Eq. (9)
U^E	excess molar internal energy
x_i	liquid mole fraction of component i
Z	lattice coordination number

Greek letters

α	parameter in MOSCED model
α	non-random parameter in the model of Shen et al. [14]
β	parameter in MOSCED model
γ_i	activity coefficient of component i
γ_i^∞	infinite dilution activity coefficient of component i
θ_i	area fraction of component i
ε	minimum potential energy
ζ	parameter in MOSCED model
ρ	number density
σ	collision diameter
τ	parameter in MOSCED model
τ_{21}, τ_{12}	binary parameters as defined by Eq. (8)
ϕ_i	segment fraction of component i
ϕ_i'	modified segment fraction of component i
ψ	parameter in MOSCED model

1. Introduction

Excess enthalpies (H^E) of non-electrolyte liquid solutions are of considerable importance for mixing or separation processes in the chemical and petroleum industries. Although there have been several accurate experimental methods that have been developed to measure directly the excess enthalpies of liquid solutions [1, 2], such measurements consume many chemicals and much time. Also, it is difficult to measure excess enthalpies for some systems, whose components are very different from each other in their molecular sizes, volatilities and viscosities, e.g. the acetone–hexadecane system, especially at a temperature that is close to the boiling point of the more volatile component in a system. Therefore, it is desirable to develop an approach for predicting excess enthalpies of mixture from other available thermodynamic properties, e.g. vapor–liquid equilibrium (VLE) or infinite dilution activity coefficients (γ_i^∞) of the same mixture.

According to the Gibbs–Helmholtz thermodynamic relation, it is possible to make cross predictions among H^E, VLE and γ_i^∞. The key point of these cross predictions is whether or not we have a suitable unified thermodynamic model. Unfortunately, the very popular local composition models (Wilson [3], NRTL [4], UNIQUAC [5]) and group contribution models (ASOG [6], UNIFAC [7]) are only suitable for describing phase equilibrium data, especially for VLE data. They cannot be used for simultaneous correlations and cross predictions between excess Gibbs free energy (G^E) data and H^E data due to their limited ability to represent large numerical values of H^E [2,8]. Improvements in simultaneously representing G^E and H^E data with these models can be obtained by increasing the adjustable temperature-dependent parameters [8–12]. However, increasing the adjustable parameters is no more than increasing the ability of these models to represent H^E data, and to correlate simultaneously G^E and H^E data. It does not improve the cross predictions between G^E and H^E data by these models. Sometimes, the cross predictions done with this kind of modified model are worse than those with the original models because the additional adjustable parameters result in more uncertainties in the determination of model parameters than with a model having fewer adjustable parameters. Besides, there are two additional problems with current group contribution models. One is that the group identification is not unique; different group contribution models artificially define different groups to represent the same molecules [13]. Another is that it is very difficult with a limited number of parameters for current group contribution models to account for isometric effects, which affect H^E data more than VLE data [12].

Recently, Shen et al. [14] have shown that their proposed solution model was capable of simultaneously representing H^E and VLE data with only three adjustable parameters for many different mixtures. In this work, we develop a new approach to predicting excess enthalpies from infinite dilution activity coefficients based on the model of Shen et al. [14]. We will also demonstrate that this approach can be used for predicting excess enthalpies of ketone–alkane systems that have large excess enthalpies, with H^E values up to 2377 J mol^{-1}.

2. Theoretical framework

Based on the unified model of Shen et al. [14], the expressions of excess molar enthalpy, excess molar Gibbs free energy, activity coefficient and infinite dilution activity coefficient for a binary system can be written as

$$H^E = \frac{Z}{2} x_1 x_2 \left[\frac{\Delta E_{21}\tau_{21}}{x_1 + x_2\tau_{21}} + \frac{\Delta E_{12}\tau_{12}}{x_2 + x_1\tau_{12}} \right] \tag{1}$$

$$\frac{G^E}{RT} = x_1 \ln\frac{\phi_1'}{x_1} + x_2 \ln\frac{\phi_2'}{x_2} + \frac{Z}{2}\left[x_1 q_1 \ln\frac{\theta_1}{\phi_1} + x_2 q_2 \ln\frac{\theta_2}{\phi_2} \right]$$

$$-\frac{Z}{2\alpha}[x_1 \ln(x_1 + x_2\tau_{21}) + x_2 \ln(x_2 + x_1\tau_{12})] \tag{2}$$

$$\ln\gamma_1 = \ln\frac{\phi_1'}{x_1} + 1 - \frac{\phi_1'}{x_1} - \frac{Z}{2}q_1\left[\ln\frac{\phi_1}{\theta_1} + 1 - \frac{\phi_1}{\theta_1}\right] + \frac{Z}{2\alpha}\left[-\ln(x_1 + x_2\tau_{21}) + x_2\left[\frac{\tau_{21}}{x_1 + x_2\tau_{21}} - \frac{\tau_{12}}{x_2 + x_1\tau_{12}}\right]\right] \tag{3}$$

$$\ln\gamma_2 = \ln\frac{\phi_2'}{x_2} + 1 - \frac{\phi_2'}{x_2} - \frac{Z}{2}q_2\left[\ln\frac{\phi_2}{\theta_2} + 1 - \frac{\phi_2}{\theta_2}\right] + \frac{Z}{2\alpha}\left[-\ln(x_2 + x_1\tau_{12}) + x_1\left[\frac{\tau_{12}}{x_2 + x_1\tau_{12}} - \frac{\tau_{21}}{x_1 + x_2\tau_{21}}\right]\right] \tag{4}$$

$$\ln\gamma_1^{\infty} = 1 - \left[\frac{r_1}{r_2}\right]^{3/4} + \ln\left[\frac{r_1}{r_2}\right]^{3/4} - \frac{Z}{2}q_1\left[1 - \frac{r_1 q_2}{r_2 q_1} + \ln\frac{r_1 q_2}{r_2 q_1}\right] + \frac{Z}{2\alpha}[1 - \ln\tau_{21} - \tau_{12}] \tag{5}$$

$$\ln\gamma_2^{\infty} = 1 - \left[\frac{r_2}{r_1}\right]^{3/4} + \ln\left[\frac{r_2}{r_1}\right]^{3/4} - \frac{Z}{2}q_2\left[1 - \frac{r_2 q_1}{r_1 q_2} + \ln\frac{r_2 q_1}{r_1 q_2}\right] + \frac{Z}{2\alpha}[1 - \ln\tau_{12} - \tau_{21}] \tag{6}$$

where

$$\Delta E_{ji} = N_0(\varepsilon_{ii} - \varepsilon_{ji}) \tag{7}$$

$$\tau_{ji} = \frac{v_{ji}}{v_j}\exp(-\alpha\Delta E_{ji}/RT) \tag{8}$$

$$v_{ji} = (v_j + v_i)/2 \tag{9}$$

$$\theta_j = \frac{x_j q_j}{\sum_k x_k q_k} \tag{10}$$

$$\phi_j = \frac{x_j r_j}{\sum_k x_k r_k} \tag{11}$$

$$\phi_j' = \frac{x_j r_j^{3/4}}{\sum_k x_k r_k^{3/4}} \tag{12}$$

N_0 *is Avogadro's constant;* v_j,q_j and r_j are the saturated liquid volume at 293.15K, the molecular surface area parameter and the molecular volume parameter of component j, respectively. They are all taken from the literature [15]. Z is the coordination number and its value is taken as 10 in this work; ε_{ji} denotes the minimum potential energy which characterizes the molecular interaction between a central molecule j and a surrounding molecule i. As in the NRTL model, the parameter α is used to characterize the tendency of the components to mix in a non-random way.

It can be seen from Eqs. (1–6) that this unified model contains three parameters (ΔE_{21}, ΔE_{12} and α), and appears to resemble formally the Wilson, NRTL and UNIQUAC models. However, this unified model is more capable of simultaneously representing G^E and H^E data than the other models mentioned. In Table 1, the results calculated with $\alpha = 0.1$ by this model and the other models are compared with the excess molar internal energy (U^E) and the excess molar Helmholtz energy (A^E) for the three kinds of equal-size Lennard-Jones mixtures considered in the computer-simulation work or Nakanishi et al. [16]. From this table, it can be demonstrated that the model of Shen et al. [14] predicts results that are fairly close to the computer-simulation results for the three different types of molecular model fluid mixtures, while the Wilson, NRTL and UNIQUAC models provide poorer predictions. Moreover, Shen et al. [14,18] have already shown that their model can simultaneously represent VLE and H^E data for many different kinds of real mixtures better than the NRTL model.

However, the model, which is capable of simultaneous correlation of G^E and H^E data, may not be suitable for cross predictions between G^E data and H^E data. One generally serious problem with these cross predictions is the uncertainty of the model parameters when these models are used to correlate VLE data or H^E data over a wide range of mixture compositions [8]. In order to avoid this uncertainty, it is better to use infinite dilution activity coefficients for determining model parameters than either VLE or H^E data. When one of the three parameters in the model of Shen et al. is predetermined through other considerations that are independent of H^E information, we can get definite solutions for the other two parameters from γ_1^∞ and γ_2^∞ based on Eqs. (5) and (6), and then use these parameters with Eq. (1) to predict H^E data for the mixture under consideration. In this work, we select α as the predetermined parameter because we find that this parameter has a regular change for one type of binary mixture. For ketone–alkane mixtures, α can be estimated from the following simple equation

$$\alpha = 0.115(NC_H) - 0.18(NC_K) + 0.43 \tag{13}$$

where (NC_H) denotes the number of skeletal carbon atoms for the alkane component, e.g. for pentane, $(NC_H) = 5$, for hexadecane, $(NC_H) = 16$, and (NC_K) is the number of skeletal carbon atoms for the ketone component, e.g. for acetone, $(NC_K) = 3$, for 2-hexanone, $(NC_K) = 6$.

Accurate experimental data of infinite dilution activity coefficients for many types of binary mixtures have been collected by Tiegs et al. [19]. However, it is still difficult to find both γ_1^∞ and γ_2^∞ for a binary mixture at one temperature in this data collection or other data sources, especially for very asymmetric systems such as the acetone–hexadecane mixture. Fortunately, Thomas and Eckert [20] have developed a simple

Table 1
Results of excess internal energy (U^E) and excess Helmholtz energy (A^E) from solution models and molecular computer simulations for equal-size Lennard-Jones mixtures

Fluid Model	$\varepsilon_{22}/\varepsilon_{11}$	$\varepsilon_{12}/\varepsilon_{11}$	$U^E/(\mathrm{J\ mol^{-1}})$[d]					$A^E/(\mathrm{J\ mol^{-1}})$[d]				
			Sim.[a]	Eq. (1)[b]	Wilson	NRTL[c]	UNIQUAC	Sim.[a]	Eq. (2)[b]	Wilson	NRTL[c]	UNIQUAC
LB-2[e]	2	$\sqrt{2}$	184	135	−1.4	4.7	−1.4	174	143	11	7	11
A − 2[f]	2	1	791	849	116	129	116	894	864	80	73	80
S − 2[g]	2	2	−1105	−911	−236	−225	−236	−944	−895	−100	−104	−100

[a] Conditions for computer simulations: $T = 120$ K, $x_1 = x_2 = 0.5, \rho = 0.75, \sigma_{11} = \sigma_{22} = \sigma_{12} = 3.405$ Å, and $(\varepsilon_{11}\varepsilon_{22})^{1/2}/k = 119.8$ K [16].

[b] α in Eqs. (1) and (2) is taken as 0.1.

[c] Following Nakanishi and Toukubo [17], α in NRTL model is fixed at 0.4.

[d] By assuming that the excess volumes for these high density mixtures are all zero, U^E and A^E are approximated by H^E and G^E in the model calculations, respectively.

[e] Lorentz–Berthelot mixture.

[f] Association model mixture.

[g] Solvation model mixture.

predictive model for infinite dilution activity coefficients (MOSCED model). This model only requires several pure component parameters, and has been successfully applied to accurately predicting 3357 γ_i^∞ data points for a wide range of mixtures [20]. Therefore, this MOSCED model is used in this work for providing values of both γ_1^∞ and γ_2^∞ at a specific temperature for the considered mixture. The MOSCED model can be expressed as

$$\ln \gamma_2^\infty = \frac{v_2}{RT}\left[(\lambda_1 - \lambda_2)^2 + \frac{q_1^2 q_2^2 (\tau_1 - \tau_2)^2}{\psi_1} + \frac{(\alpha_1 - \alpha_2)(\beta_1 - \beta_2)}{\zeta_1}\right] + \left[\ln (v_2/v_1)^{(aa)} + 1 - (v_2/v_1)^{(aa)}\right] \tag{14}$$

where v_2 is the liquid molar volume at 20°C. The expression for γ_1^∞ is obtained by interchanging the subscripts. The MOSCED parameters τ, α, β, ψ, ζ and $(a\ a)$ are temperature dependent according to the following equations

$$\tau_T = \tau_{293}\left[\frac{293}{T}\right]^{0.4} \tag{15}$$

$$\alpha_T = \alpha_{293}\left[\frac{293}{T}\right]^{0.8} \tag{16}$$

$$\beta_T = \beta_{293}\left[\frac{293}{T}\right]^{0.8} \tag{17}$$

$$\psi = \mathrm{POL} + 0.011\alpha_T \beta_T \tag{18}$$

$$t = (293/T)^2 \tag{19}$$

$$\zeta = 0.68(\mathrm{POL} - 1) + \{3.4 - 2.4\exp[-0.023(\alpha_{293}\beta_{293})^{1.5}]\}^t \tag{20}$$

$$\mathrm{POL} = q^4[1.15 - 1.15\exp(0.020\tau_T^3)] + 1 \tag{21}$$

$$(aa) = 0.953 - 0.00968(\tau_2^2 + \alpha_2\beta_2) \tag{22}$$

The parameters v, λ, τ, q, α, β, ψ, ζ and $(a\ a)$ are tabulated by Thomas and Eckert [20] for about 145 compounds. For other compounds, the parameters can be estimated from approximate relations valid for some classes of compounds [20].

3. Predicted results and discussions

The 35 sets of excess enthalpy data for 23 binary ketone–alkane systems have been predicted by the above approach with estimated values of γ_1^∞ and γ_2^∞ from the MOSCED model. The predicted results are summarized in Table 2, and typical results are shown in Figs. 1 and 2.

From Table 2 and Figs. 1 and 2, it can be seen that the predicted results are very satisfactory. The average relative deviation of the predicted results for 500 data points is only 8.20%. Even for systems having large H^E values, such as the acetone–hexadecane system, our predicted results are still very good. The average absolute deviation of our predicted results for the acetone–hexadecane system is 141.1 J mol^{-1}, while that of the results correlated by the empirical four-parameter Redlich–Kister model is 55.43 J mol^{-1} [2]. Our predicted results are also comparable with the results of the modified UNIFAC models [11, 12] which usually have six adjustable parameters. Furthermore, the proposed approach is quite simple; the ketone–alkane mixtures considered in this work include a wide range of molecular sizes for both ketone (from acetone to 2-hexanone) and alkane (from pentane to hexadecane). Also, the proposed approach does not have any uncertainty due to using infinite dilution activity coefficients.

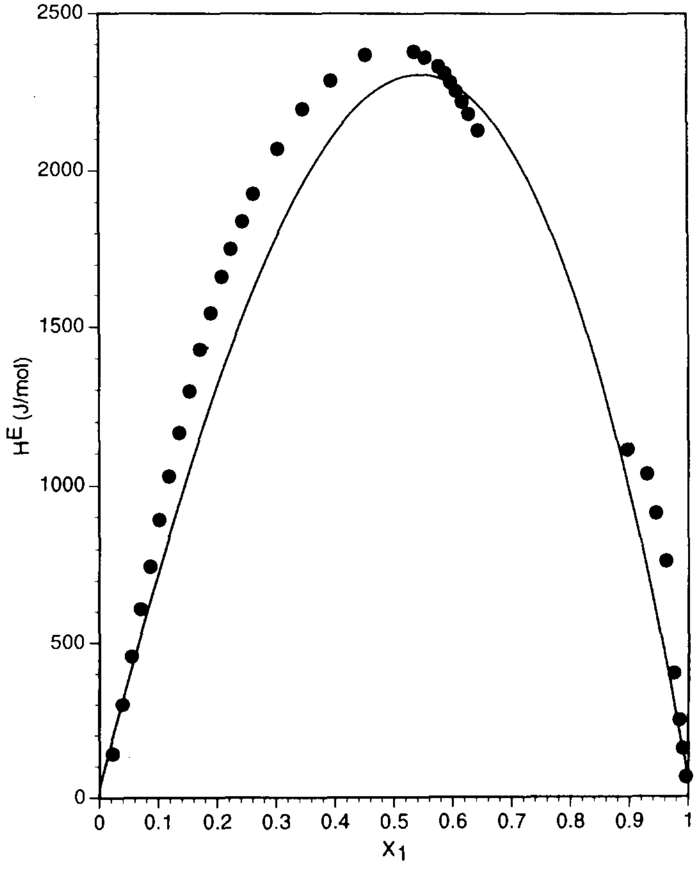

Fig. 1. Excess enthalpies of acetone (1)–hexadecane (2) at 298.15 K: ●, experimental [27]; ———, predicted.

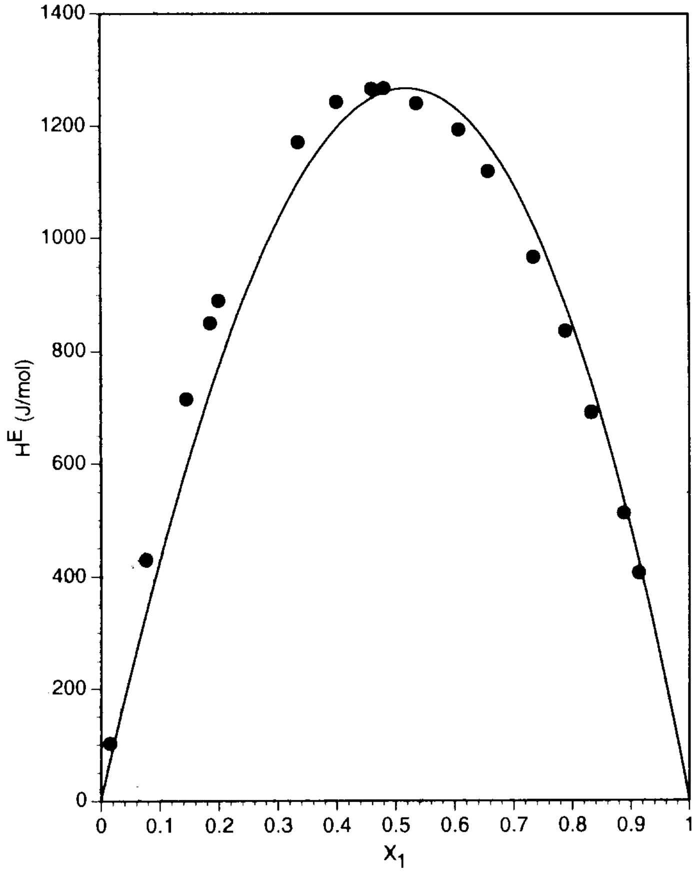

Fig. 2. Excess enthalpies of 2-hexanone(1)–decane(2) at 298.15 K: ●, experimental [35]; ———, predicted.

When accurate experimental values of infinite dilution activity coefficients for the considered mixture are available, we can use them directly to predict H^E data of this mixture instead of using the values estimated from the MOSCED model. Table 3 shows the results of predicted excess enthalpies for five systems whose experimental infinite dilution activity coefficients can be found in the literature. From Table 3, it can be seen that these predicted results are also very good. Comparing these results with those from the MOSCED model for the same set of excess enthalpy data, we can see that better results can be obtained from experimental γ_1^∞ and γ_2^∞ values than from the MOSCED model for the acetone–pentane (293.20 K) and acetone–hexane (298.15 K) systems, while the results of the acetone–heptane (298.15 K), butanone–hexane (298.15 K) and butanone–heptane (298.15 and 318.15 K) systems from experimental γ_1^∞ and γ_2^∞ values are worse than those from the MOSCED model. For 85 data points of these five systems, the average relative deviation of the predicted results from the MOSCED model is 10.63%, while that of the results from experimental γ_1^∞ and γ_2^∞ values is 9.83%. The latter is only slightly better than the former.

Table 2
Results of predicted excess enthalpies of ketone (1)–alkane (2) systems with estimated values of γ_1^∞ and γ_2^∞ from the MOSCED model

System (1 2)	T_h/K[a]	γ_1^∞	γ_2^∞	α	ΔE_{21}/ (J mol^{-1})	ΔE_{12}/ (J mol^{-1})	No. of data points	Abs. arith. mean deviations			Ref. of data
								H^E_{max}/ (J mol^{-1})[b]	ΔH^E/ (J mol^{-1})[c]	δH^E(%)[d]	
Acetone–pentane	253.15	15.55	8.55	0.4650	2814.81	−1393.66	9	1281.20	236.48	18.46	[21]
	293.20	8.11	5.41	0.4650	2930.52	−1603.40	13	1450.00	380.53	26.24	[22]
Acetone–hexane	253.15	15.14	10.84	0.5800	2240.60	−774.409	9	1352.30	95.01	7.03	[21]
	273.15	10.57	8.14	0.5800	2274.12	−856.245	9	1465.40	87.53	5.98	[21]
	293.15	7.88	6.43	0.5800	2305.02	−926.506	9	1557.50	156.00	10.02	[21]
	298.15	7.38	6.11	0.5800	2312.30	−942.431	9	1576.80	126.14	8.00	[23]
Acetone–heptane	298.15	7.19	7.23	0.6950	1917.69	−433.539	6	1707.00	68.55	4.02	[24]
	323.15	5.41	5.58	0.6950	1936.22	−482.497	12	1782.00	98.68	5.53	[25]
Acetone–decane	313.15	5.55	9.50	1.0400	1423.47	469.301	12	1885.00	206.75	10.96	[25]
Acetone–dodecane	303.15	5.92	14.72	1.0400	1318.80	848.063	5	2081.00	78.16	3.76	[26]
	313.15	5.25	12.44	1.2700	1317.88	835.635	12	2010.00	197.62	9.83	[25]
Acetone–tetradecane	313.15	5.02	16.29	1.5000	1270.21	1118.97	12	2078.00	147.55	7.10	[25]
Acetone–hexadecane	298.15	5.73	29.38	1.7300	1263.71	1383.33	36	2377.00	141.08	5.94	[27]
	298.15	5.73	29.38	1.7300	1263.71	1383.33	10	2376.40	163.53	6.88	[28]
Butanone–hexane	298.15	4.61	4.05	0.4000	2206.39	−1216.41	19	1259.10	197.55	15.69	[29]
Butanone–heptane	298.15	4.48	4.58	0.5150	1629.18	−552.393	20	1338.90	58.98	4.41	[30]
	298.15	4.48	4.58	0.5150	1629.18	−552.393	10	1323.60	57.14	4.32	[31]
	318.20	3.76	3.93	0.5150	1601.98	−540.467	8	1328.00	61.74	4.65	[32]
	323.20	3.62	3.80	0.5150	1594.97	−536.446	6	1382.00	43.38	3.14	[32]
Butanone–octane	298.15	4.36	5.17	0.6300	1310.74	−110.313	20	1408.50	62.25	4.42	[30]
Butanone–decane	298.15	4.13	6.54	0.8600	1023.19	432.107	20	1545.00	126.05	8.16	[30]
Butanone – dodecane	298.15	3.90	8.15	1.0900	922.187	757.281	14	1659.00	190.86	11.50	[33]
Butanone–hexadecane	298.15	3.52	12.37	1.5500	874.032	1173.27	12	1860.00	139.04	7.48	[33]
3-Pentanone–heptane	293.15	3.88	3.77	0.3350	1765.66	−902.108	12	1075.20	78.16	7.27	[34]
	298.15	3.72	3.64	0.3350	1752.34	−894.182	20	1084.00	60.82	5.61	[30]
3-Pentanone–octane	298.15	3.63	4.04	0.4500	1210.20	−245.994	20	1141.90	62.83	5.50	[30]
3-Pentanone–decane	298.15	3.45	4.93	0.6800	807.416	397.411	20	1261.50	135.14	10.71	[30]
2-Pentanone–heptane	298.15	3.76	3.65	0.3350	1797.06	−935.984	20	1143.00	110.80	9.69	[30]
	298.15	3.76	3.65	0.3350	1797.06	−935.984	10	1128.30	86.95	7.70	[31]

2-Pentanone–octane	298.15	3.67	4.06	0.4500	1239.59	− 274.654	20	1203.80	43.23	3.59	[30]
2-Pentanone–decane	298.15	3.50	4.98	0.6800	822.718	383.627	20	1335.20	97.21	7.28	[30]
2-Hexanone–heptane	298.15	3.33	3.05	0.1550	3021.07	− 2269.28	10	996.00	196.51	19.73	[31]
2-Hexanone–octane	298.15	3.27	3.35	0.2700	1489.24	− 700.526	19	1133.00	128.24	11.32	[35]
2-Hexanone–nonane	298.15	3.20	3.67	0.3850	920.416	− 29.4634	20	1204.00	57.49	4.78	[35]
2-Hexanone–decane	298.15	3.13	4.01	0.5000	707.255	304.466	17	1268.00	55.47	4.37	[35]

[a] T_h denotes the temperature of excess enthalpy data.

[b] H^E_{max} is the maximum value in one set of excess enthalpy data.

[c] $\Delta H^E = (1/N_p)\sum_i |H^E_{exp} - H^E_{cal}|_i$; where N_p is the number of experimental data points.

[d] $H^E = (1/N_p)\sum_i |(H^E_{exp} - H^E_{cal})/H^E_{max}|_i \times 100\%$.

Table 3
Results of predicted excess enthalpies for ketone (1)–alkane (2) systems with experimental γ_1^∞ and γ_2^∞

System (1–2)	T_γ/K[a]	γ_1^∞	γ_2^∞	Ref.	α	ΔE_{21}/ (J mol^{-1})	ΔE_{12}/ (J mol^{-1})	T_h/K	N_p	Abs. arith. mean deviations			Ref. of data
										ΔH^E/ (J mol^{-1})	δH^E (%)	$\delta H^{E\,b}$(%)	
Acetone–pentane	303.11	7.07	5.84	[36]	0.4650	2402.18	− 1130.31	293.20	13	189.94	13.10	26.24	[21]
Acetone–hexane	298.15	6.68	6.62	[37]	0.5800	1897.80	− 550.449	298.15	9	52.42	3.33	8.00	[23]
Acetone–heptane	298.15	7.40	7.10	[37]	0.6950	2001.90	− 515.281	298.15	6	70.30	4.12	4.02	[24]
Butanone–hexane	298.15	4.53	4.00	[36]	0.4000	2181.42	− 1200.78	298.15	19	198.88	15.80	15.69	[29]
Butanone–heptane	313.15	4.41	4.12	[36]	0.5150	2002.77	− 901.763	298.15	20	119.20	8.90	4.41	[30]
	313.15	4.41	4.12	[36]	0.5150	2002.77	− 901.763	298.15	10	101.16	7.64	4.32	[31]
	313.15	4.41	4.12	[36]	0.5150	2002.77	− 901.763	318.20	8	92.82	7.00	4.65	[32]

[a] T_γ denotes the temperature of experimental infinite dilution activity coefficient.

[b] Obtained from the values of γ_1^∞ and γ_2^∞ estimated by the MOSCED model (Table 2).

It should be pointed out that the proposed approach is suitable not only for ketone–alkane systems, but also for other types of systems. The key to applying this approach to other types of systems is to find a suitable expression of the parameter α for a specific type of system. The use of the proposed approach for other types of systems seems promising.

4. Conclusion

This work provides a simple expression of the parameter α in the model of Shen et al. [14] for ketone–alkane systems. With this expression and two infinite dilution activity coefficients, γ_1^∞ and γ_2^∞, of a ketone (1)–alkane (2) system, the excess enthalpies of this system can be accurately predicted by the model of Shen et al. This proposed approach does not have any uncertainty due to using infinite dilution activity coefficients. It has been used for predicting excess enthalpies of 23 ketone–alkane systems. For 500 total data points, the average relative deviation is 8.20%.

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References

[1] K.N. Marsh, in M.L. McGlashan (Ed.), Chemical Thermodynamics, Vol. 2, Special Periodical Reports, The Chemical Society, London (1978) pp. 1–45.

[2] C. Christensen, J. Gmehling, P. Rasmussen and U. Weidlish, Heats of Mixing Data Collection, Binary Systems, DECHEMA Chemistry Data Ser., Vol. III, Part 1, DECHEMA, Frankfurt/Main, Germany, (1984).

[3] G.M. Wilson, J. Am. Chem. Soc., 86, (1964) 127–130.

[4] H. Renon and J.M. Prausnitz, AICHE J., 14 (1968) 135–144.

[5] D.S. Abrams and J.M. Prausnitz, AICHE J., 21 (1975) 116–128.

[6] K. Kojima and K. Tochigi, Prediction of Vapor–Liquid Equilibrium by the ASOG method, Elsevier, 1979.

[7] A. Fredenslund, J. Gmehling and P. Rasmussen, Vapor–Liquid Equilibrium Using UNIFAC, Elsevier, 1977.

[8] G.L. Nicolaids and C.A. Eckert, Ind. Eng. Chem. Fundam., 17 (1978) 331–340.

[9] I. Nagata, T. Ohta and T. Takahashi, J. Chem. Eng. Jpn., 5 (1972) 227–231.

[10] I. Nagata and T. Yamada, Ind. Eng. Chem. Process Des. Dev., 13 (1974) 47–53.

[11] B.L. Larsen, P. Rasmussen and A. Fredenslund, Ind. Eng. Chem. Res., 26 (1987) 2274–2286.

[12] J. Gmehling, J. Li and M. Schiller, Ind. Eng. Chem. Res., 32 (1993) 178–193.

[13] H.S. Wu and S.I. Sandler, Ind. Eng. Chem. Res., 30 (1991) 881–889.

[14] S. Shen, Y. Wang and J. Shi, International Symposium on Thermodynamics in Chemical Engineering and Industry, Beijing, China, May 30–June 2, 1988, pp. 313–318.

[15] J. Gmehling, U. Onken and W. Arlt, Vapor–Liquid Equilibrium Data Collection, Aldehydes and Ketones, Ethers, DECHEMA Chemistry Data Ser., DECHEMA Frankfurt/Main, Germany. Vol. I, Part 3 + 4, 1979.

[16] K. Nakanishi, S. Okazaki, K. Ikari, T. Higuchi and H. Tanaka, J. Chem. Phys., 76 (1982) 629–636.
[17] K. Nakanishi and K. Toukubo, J. Chem. Phys., 70 (1979) 5848–5850.
[18] S. Shen, Y. Wang., J. Shi, G.C. Benson and B.C.-Y. Lu, J. Chem. Eng. Data, 37 (1992) 400–402.
[19] D. Tiegs, J. Gmehling, A. Medina, M. Soares, J. Bastos, P. Alessi and I. Kikic, Activity Coefficients at Infinite Dilution, DECHEMA Chemistry Data Ser., DECHEMA Frankfurt/Main, Germany, Vol. IX, Part 1, 1986.
[20] E.R. Thomas and C.A. Eckert, Ind. Eng. Chem. Process Des. Dev., 23 (1984) 194–209.
[21] K. Schaefer and F.J. Rohr, Z. Phys. Chem. (Frankfurt am Main), 24 (1960) 130–151.
[22] K. Schaefer, Int. Data Series, Sel. Data Mixtures Ser. A, 16 (1978) 76.
[23] S. Murakami, K. Amaya and R. Fujishiro, Bull. Chem. Soc. Jpn. 37 (1964) 1776–1780.
[24] D.O. Hanson and M. Van Winkle, J. Chem. Eng. Data, 5 (1960) 30–34.
[25] S. Shen, Y. Wang, J. Shi, G.C. Benson and B.C.-Y. Lu, J. Chem. Thermodyn., 22 (1990) 387–392.
[26] J. Gaube, L. Krenzer, L.L. Hang and K. Scharr, Private communication to Prof. Gmehling, in J. Gmehling and T. Holderbaum (Ed.), Heats of Mixing Data Collection, Binary and Multicomponent Systems (Supplement 1), DECHEMA Chemistry Data Ser., DECHEMA Frankfurt/Main, Germany, Vol. III, Part 3, (1989) p. 1750.
[27] D. Kuchenbecker, Thesis, Leipzig, 1980.
[28] U. Messow, U. Doye, S. Kuntzsch and D. Kuchenbecker, Z. Phys. Chem. (Leipzig), 258 (1977) 90–96.
[29] O. Kiyohara, G.C. Benson and J.-P.E. Grolier, J. Chem. Thermodyn., 9 (1977) 315–323.
[30] O. Kiyohara, Y.P. Handa and G.C. Benson, J. Chem. Thermodyn., 11 (1979) 453–460.
[31] O. Dusart, S. Piekarski and J.-P.E. Grolier, J. Chim. Phys., 76 (1979) 433–437.
[32] R. Fuchs, L. Krenzer and J. Gaube, Ber. Bunsenges, Phys. Chem., 88 (1984) 642–649.
[33] U. Messow, U. Doye, S. Kuntzsch and D. Kuchenbecker, Z. Phys. Chem. (Leipzig), 259 (1978) 664–666.
[34] G. Geiseler and H. Koehler, Ber Bunsenges. Phys. Chem., 72 (1968) 697–706.
[35] J.L. Legido, R. Bravo and M.I. Paz Andrade, J. Chem. Thermodyn., 18 (1986) 21–26.
[36] L. Dallinga, M. Schiller and J. Gmehling, J. Chem. Eng. Data, 38 (1993) 147–155.
[37] J. Bao, L. Hang and S. Han, J. Chem. Thermodyn., 26 (1994) 673–680.