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Analysis of excess heat capacities of 1-alkanol + *n*-alkane mixtures using the Nitta–Chao model

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Abstract

The Nitta–Chao model was used to predict the excess heat capacities of the following mixtures ($n+m$) of 1-alkanol (C_mH_{2m+1})+ *n*-alkane (C_nH_{2n+2}): 2+7, 2+12, 3+7, 4+7, 4+12, 5+7, 6+6, 6+12, 6+16, 10+7, 10+10 and 10+12 at 298.15 K and 3+6 and 3+7 at 185, 200, 220, 250, 270 and 295 K.

INTRODUCTION

One of the main characteristics of the thermodynamic properties of 1-alkanol–*n*-alkane mixtures is the outstanding symmetry presented by the functions of excess compared with the molar fraction and the dependence of such symmetry on the temperature. This marked deviation from ideality is due to the formation of associations by hydrogen bonds both in impure 1-alkanol and in the solution.

Any theoretical model which tries to describe the behaviour of these mixtures has to take into account the chemical association that is the cause of the existence of "structure" in the mixture.

The most sensitive indicator of "structure" is the calorific capacity and the calorific capacity of excess, C_p^E. In spite of the existence of enough experimental C_p and C_p^E data of mixtures of 1-alkanol and *n*-alkane [1–6] we have found only one reference to a theoretical treatment [2].

As a theoretical framework for interpreting the heat capacity data on 1-alkanol–*n*-alkane mixtures, we have chosen the Nitta–Chao model [7], because this theory includes a "combinatorial" or "chemical" term and a

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dispersive term for the lattice energy. The chemical term is related to the hydrogen bond contribution to lattice energy.

THEORETICAL MODEL

The following brief sketch of the model is intended to make clear the physical meaning of its adjustable parameters. The cell partition function for a pure liquid or a mixture is (Lee et al. [8])

$$Q = g\left(\prod_{\mathrm{A}} \Psi_{\mathrm{A}}^{N_{\mathrm{A}}}\right) \exp(-E/kT) \tag{1}$$

where the molecular cell partition function Ψ_{A} is given in terms of the contributions of the constituent groups by

$$\Psi_{\mathrm{A}} = \prod_{i} \Psi_i^{n_i^{\mathrm{A}} c_i} \tag{2}$$

where the number of external degrees of freedom of group i, namely c_i, is a characteristic parameter of the model. Ψ_i is given by the Carnahan–Starling hard sphere equation of state [9]:

$$\Psi_i = \tilde{v} \exp\left[-(4\tilde{v} - 3)/(\tilde{v} - 1)^2\right] \tag{3}$$

where $\tilde{v} = V/V^*$ is the reduced volume. The temperature dependence of the hard core volume of group i, V_i^*, is given by the empirical expression

$$V_i^* = V_{i0}^* \exp\left[a_i\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{4}$$

where V_{i0}^* is the hard core volume at the temperature T_0 (normally 298.15 K). Both a_i and V_{i0}^* are characteristic parameters that are determined by fitting the theoretical equations to experimental data.

In terms of the contributions of the component groups, the lattice energy E is given by

$$E = \sum_{i \geq j}\sum N_{ij} \Phi_{ij} \tag{5}$$

where Φ_{ij}, the energy of pairwise interaction between groups, is the sum of a dispersive term and a chemical term:

$$\Phi_{ij} = -\left(\varepsilon_{ij}/\tilde{v}\right) \exp(\kappa/\tilde{v}) - \sigma_{ij} \tag{6}$$

ε_{ij} being the dispersive interaction energy parameter and κ a constant whose value is 0.7.

The chemical association energy σ_{ij} is temperature dependent and is given by

$$\frac{\sigma_{ij}}{T} = \frac{\sigma_{ij}^0}{T_0} + \sigma_{ij}'\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{7}$$

where σ_{ij}^0 and σ_{ij}' are characteristic parameters of this model.

TABLE 1

Characteristic parameter for the Nitta–Chao model calculated by Nitta et al. [7] and by Fernandez et al. [10] [a]

Group	V_{i0}^* ($cm^3\ mol^{-1}$)	a_i (K)	c_i	Q_i	ε_{ii} ($J\ mol^{-1}$)
$-CH_3$	13.46	23.7	0.338	6.71	2515
$-CH_2$	10.25	23.7	0.093	4.27	2515
-OH (O)	8.10 [a]	10.0 [a]	0.250 [a]	3.62	5983 [a]
-OH (H)				1.00	

[a] The following values were also obtained from ref. 10: $\varepsilon_{ij}(CH_3, OH)$ 3138 J mol^{-1}; σ^0(O, H) 13263 J mol^{-1}; σ'(O, H) 20000 J mol^{-1}.

For the number of contacts N_{ij} the quasi-chemical approximation is used. The expression for the thermodynamics properties of both pure liquids and mixtures are derived by the standard methods of statistical thermodynamics.

The molar heat of mixing is strictly given by

$$H^E = U_{conf} - \sum_A x_A U_{A0\,conf} \tag{8}$$

where

$$U_{conf} = kT^2(\partial \ln Q/\partial T)_{V,N} \tag{9}$$

TABLE 2

Excess heat capacities at 298.15 K of $C_mH_{2m+1}OH + C_nH_{2n+2}$ mixtures; experimental values and predicted values using the Nitta–Chao model differences

System: $m+n$	N	C_p^E ($J\ mol^{-1}\ K^{-1}$) Exp. 0.2 [a]	Exp. 0.5 [a]	Nitta–Chao 0.2 [a]	Nitta–Chao 0.5 [a]	σC_p^E	δC_p^E (%)	Ref.
2+7	15	13.53	10.54	11.95	9.03	1.32	0.17	1
2+12	8	13.84	12.82	16.14	13.37	1.21	0.12	2
3+7	14	12.94	12.54	11.77	8.84	2.50	0.27	1
4+7	8	12.89	12.69	11.57	8.67	2.59	0.27	2
4+12	8	16.87	15.05	15.69	12.99	2.04	0.19	1
5+7	8	12.05	11.68	11.37	8.51	2.07	0.27	3
6+6	10	10.36	9.90	10.17	7.39	1.54	0.23	4
6+7	8	11.41	10.69	11.17	8.35	1.50	0.19	2
6+8	8	12.74	12.59	12.09	9.25	2.32	0.25	2
6+10	9	13.43	12.05	13.76	10.97	1.15	0.13	2
6+12	9	15.48	14.03	15.24	12.61	1.01	0.11	2
6+16	8	15.50	13.42	17.76	15.71	1.57	0.12	2
10+7	8	9.73	7.45	10.43	7.78	0.64	0.08	2
10+10	7	10.80	8.64	12.95	10.30	1.02	0.11	2
10+12	8	13.24	10.60	14.37	11.86	0.94	0.09	2

[a] Value of x.

The excess heat capacity is given by

$$C_p^{\mathrm{E}} = (\partial H^{\mathrm{E}}/\partial T)_{P,N} \tag{10}$$

Values of these groups and interaction constants are tabulated in Table 1.

RESULTS AND DISCUSSION

In order to verify the validity of the Nitta–Chao model to predict the C_p^{E} values of mixtures of 1-alkanol–*n*-alkane, we have selected in the bibliography a series of systems from which we can observe the variation of C_p^{E} with the number of carbon atoms of both the 1-alkanol and the *n*-alkane.

The characteristic parameters employed to apply the theory were the original ones of Nitta et al. for the groups CH_3 and CH_2 [7] whereas the values calculated by Fernandez et al. [10] were taken for the group OH. The method employed for the C_p^{E} calculation was the numerical derivation of H^{E}, calculated according to Nitta's model along the whole interval of molar fractions at several close temperatures.

The results of the comparison of the experimental results and the predictions of the Nitta–Chao model are presented in Table 2 and Fig. 1. These allow us to appreciate that there is a reproduction of the increase in C_p^{E} with the *n*-alkane chain (Fig. 2) with a fixed 1-alkanol as solvent, as well as the reduction of C_p^{E} with increase of the 1-alkanol chain (Fig. 3) whilst maintaining the same alkane as solvent. At the same time, this

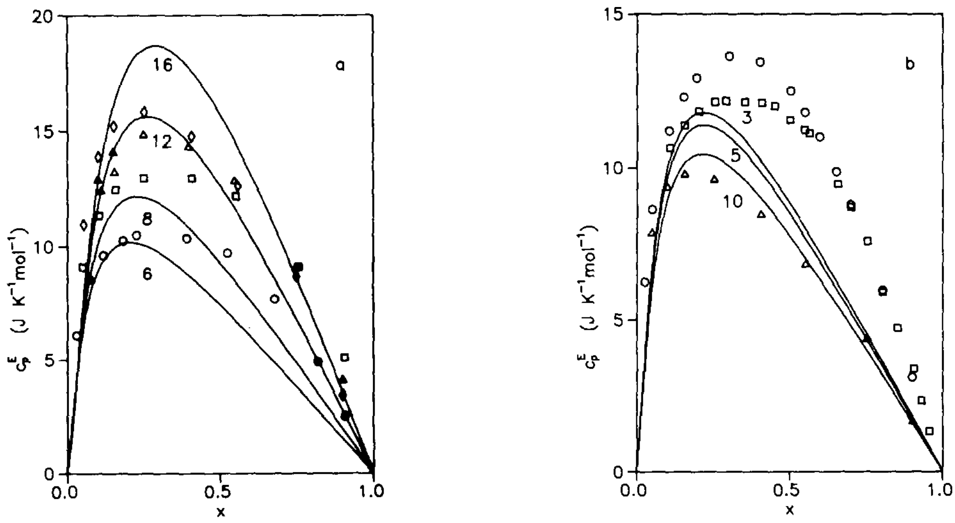

Fig. 1. Nitta et al. [7] model predictions for C_p^{E} of $C_nH_{2n+1}OH + C_mH_{2m+2}$ at 298.15 K. The curves are the predicted excess capacities. Experimental points: (1) ○, $n = 6$ $m = 6$ [8]; □, $n = 8$ $m = 6$ [6]; △, $n = 12$ $m = 6$ [6]; ◇, $n = 16$ $m = 6$ [6]; (b) ○, $n = 7$ $m = 3$ [5]; □, $n = 7$ $m = 5$ [7]; △, $n = 7$ $m = 3$ [6].

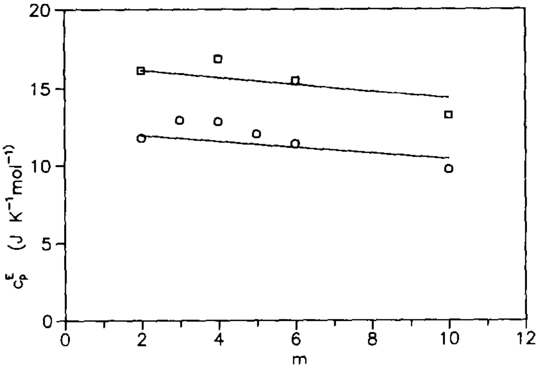

Fig. 2. C_p^E values at $x_1 = 0.2$ values against m of the mixtures $C_nH_{2n+1}OH + C_mH_{2m+2}$ at 298.15 K. Experimental points: ○, $n = 12$; □, $n = 7$. Lines are predicted values.

model gives an account of the asymmetry of the curves towards low concentrations in 1-alkanol, the deviation between theoretical and experimental values being about 20%.

Kalinowska et al. [5,6] have measured C_p^E values of the systems 1-propanol + (n-hexane and n-heptane) over a wide temperature interval (184–330 K). However, they do not offer parameters for adjusting the experimental results, so we have fitted a function of the form

$$C_p^E = \sum A_i T^i \tag{11}$$

where i is the total number of coefficients. The results were fitted for each molar fraction by the ordinary (unweighted) least-squares method. The parameters, A_i, and standard deviations, s, of the fit are listed in Table 3. The number of coefficients, i, was determined in each case using an F-test [11]. Using these parameters we calculated C_p^E at six temperatures, and compared the results with the values obtained by means of the Nitta–Chao

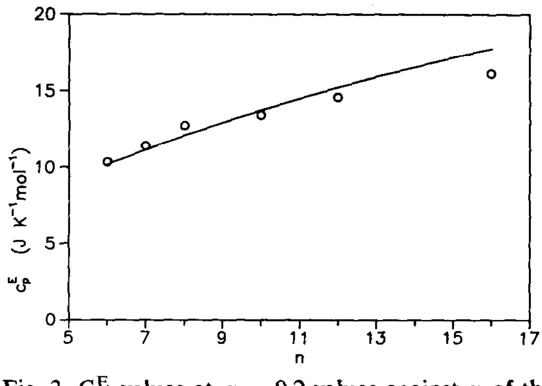

Fig. 3. C_p^E values at $x_1 = 0.2$ values against n of the mixtures $C_nH_{2n+1}OH + C_mH_{2m+2}$ at 298.15 K. Experimental points: ○, $m = 6$. The line represents predicted values.

TABLE 3

Coefficients A_i of eqn. (11) and standard deviations s

x	A_0	A_1	A_2	A_3	A_4	s
(x)Propan-1-ol + $(1-x)$hexane						
0.0258	64.97	−0.8415	3.411×10^{-3}	-4.131×10^{-6}		0.36
0.0480	19.73	−0.2184	6.053×10^{-4}			0.23
0.0760	−279.0	4.781	-3.023×10^{-2}	8.299×10^{-5}	-8.207×10^{-8}	0.19
0.1031	−479.0	8.488	-5.579×10^{-2}	1.605×10^{-5}	-1.688×10^{-7}	0.25
0.2050	43.23	−0.4500	1.176×10^{-3}			0.25
0.3081	35.64	−0.3689	9.834×10^{-4}			0.38
0.5005	−838.8	14.18	-8.899×10^{-2}	2.449×10^{-4}	-2.477×10^{-7}	0.26
0.6477	−679.9	11.83	-7.662×10^{-2}	2.180×10^{-4}	-2.283×10^{-7}	0.22
0.8010	28.12	−4.769	2.980×10^{-2}	-8.190×10^{-5}	8.456×10^{-8}	0.20
(x)Propan-1-ol + $(1-x)$heptane						
0.0225	−444.6	7.859	-5.171×10^{-2}	1.496×10^{-4}	-1.597×10^{-7}	0.12
0.0707	−376.5	6.468	-4.132×10^{-2}	1.156×10^{-4}	-1.181×10^{-7}	0.13
0.1273	−333.8	5.450	-3.280×10^{-2}	8.544×10^{-5}	-7.941×10^{-8}	0.14
0.2075	−216.4	3.590	2.204×10^{-2}	5.848×10^{-5}	-5.478×10^{-8}	0.10
0.3551	−400.9	6.628	-4.069×10^{-2}	1.089×10^{-4}	1.052×10^{-7}	0.11
0.4957	−253.5	4.184	-2.580×10^{-2}	6.923×10^{-5}	6.626×10^{-8}	0.07
0.5956	−293.2	4.698	-2.798×10^{-2}	7.223×10^{-5}	-6.648×10^{-8}	0.10
0.7513	−51.98	0.6537	-2.964×10^{-3}	4.802×10^{-6}		0.19

TABLE 4

Excess heat capacities of propan-1-ol + (n-hexane and n-heptane): experimental values were obtained using eqn. (11) and predicted values from the Nitta–Chao model

T (K)	C_p^E (J mol^{-1} K^{-1}) Exp.		Nitta–Chao	
Propan-1-ol + hexane				
	0.2050 [a]	0.5005 [a]	0.2050 [a]	0.5005 [a]
185	0.21	−0.63	−0.93	−1.18
200	0.25	0.55	−0.53	−0.93
220	1.12	1.19	0.30	−0.33
250	4.19	3.33	2.98	1.51
270	7.41	6.40	5.90	3.64
295	12.76	11.11	10.24	7.36
Propan-1-ol + heptane				
	0.2067 [a]	0.4957 [a]	0.2067 [a]	0.4957 [a]
185	−0.41	−1.73	−0.95	−1.26
200	0.26	−0.87	−0.54	−0.98
220	1.12	0.19	0.43	−0.31
250	3.48	2.85	3.40	1.75
270	6.25	5.81	6.59	4.13
295	11.23	10.92	11.22	8.26

[a] Value of x.

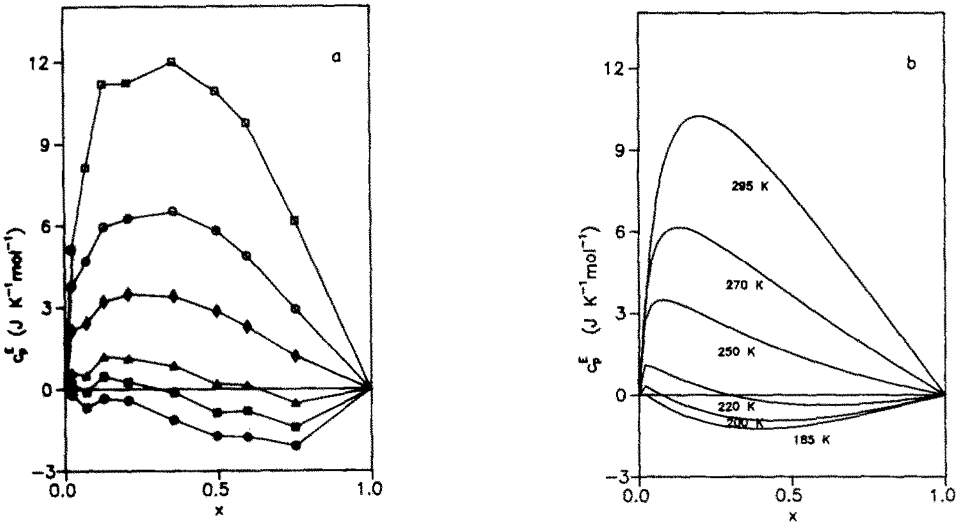

Fig. 4. C_p^E of $C_3H_7OH+C_6H_{14}$. (a) Experimental points calculated from eqn. (11): •, 185 K; ■, 200 K; △, 220 K; ◇, 250 K; ○, 270 K; □, 295 K. (b) Predicted values of Nitta–Chao model.

[7] model (Table 4, Figs. 4 and 5). We can observe that the model predicts the increase in C_p^E when the temperature is increased and so the existence of curves with positive and negative values, at low temperatures.

The Nitta–Chao model appears to be a valid method by which to describe the thermodynamic behaviour of the mixtures since it can repro-

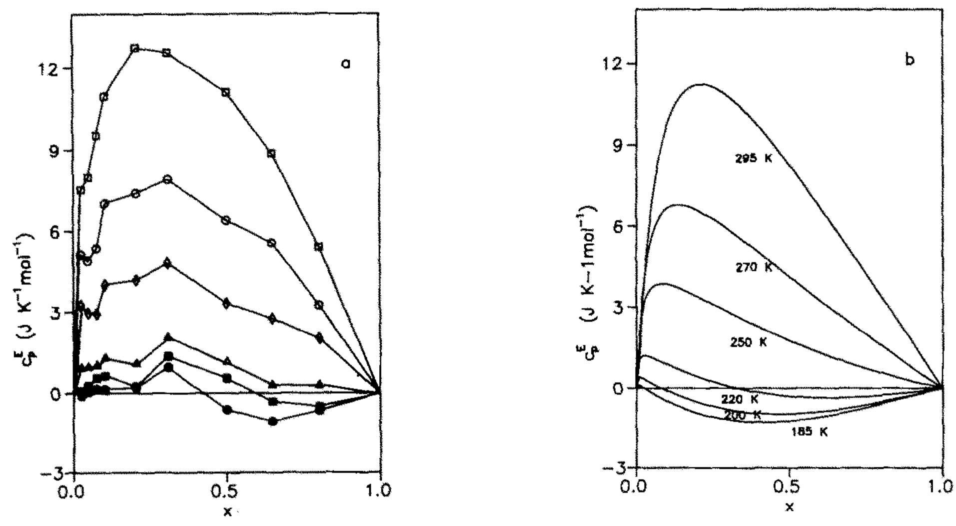

Fig. 5. C_p^E of $C_3H_7OH+C_7H_{16}$. (a) Experimental points calculated from eqn. (11): •, 185 K; ■, 200 K; △, 220 K; ◇, 250 K; ○, 270 K; □, 295 K. (b) Predicted values of Nitta–Chao model.

duce fairly well a second-order magnitude parameter such as C_p^E, closely related to the existence of structures in the solutions.

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