Thermochimica Acta, 179 (1991) 347–350
Elsevier Science Publishers B.V., Amsterdam

Note

EXCESS VOLUMES OF CYCLOALKANOL + *n*-ALKANE SYSTEMS IN TERMS OF AN ASSOCIATED SOLUTION THEORY WITH A FLORY EQUATION OF STATE CONTRIBUTION

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(Received 3 August 1990)

A model [1–5] for the excess volumes of binary systems comprising a self-associated component and an inert solvent was applied to some cycloalkanol + *n*-alkane systems. The estimated excess volumes correlate well with experimental results [6,7] for systems formed by mixing a cycloalkanol (C_5, C_6) with an *n*-alkane (C_6–C_8, C_{10}, C_{12}).

RESULTS AND DISCUSSION

In our model, the excess molar volume V^E is expressed as the sum of a chemical contribution described by an athermal associated solution of the Mecke–Kempter type, and a physical contribution obtained from the Flory equation of state. Details of the model and the relevant equations are given in our earlier publications [1–3]. The same notation is adopted here.

The characteristic values (pressure p^*, molar volume V^* and temperature T^*) needed to evaluate the Flory equation of state contribution were calculated as previously [1,5,8] from the properties (molar volume V°, isobaric thermal expansivity α_p°, and isothermal compressibility κ_T°) of the pure components, and are summarized in Table 1. A procedure, analogous to that used for pyridine base + *n*-alkane systems [3,4], was followed to establish the values of the four model parameters: the molar enthalpy Δh_H°, molar entropy Δs_H°, and molar volume Δv_H° of H-bond formation, and the Flory exchange interaction parameter X_{12}. The values $\Delta h_H^\circ = -24.4$ kJ mol^{-1} and $\Delta v_H^\circ = -10$ cm^3 mol^{-1} used previously for alkanols [1,2,5] were adopted in the present calculations.

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TABLE 1

Molar volume V°, isobaric thermal expansivity α_p°, and isothermal compressibility κ_T° for the component liquids at 298.15 K, and characteristic values of the pressure p^*, molar volume V^*, and temperature T^* obtained from the Flory formalism

	V° (cm^3 mol^{-1})	α_P° (kK^{-1})	κ_T° (TPa^{-1})	p^* (J cm^{-3})	V^* (cm^3 mol^{-1})	T^* (K)
Cyclopentanol [5]	91.342	0.829	620.0	585.2	75.392	5829
Cyclohexanol [5]	105.977	0.804	590.7	590.3	87.868	5939
n-Hexane [1]	131.597	1.387	1703.9	424.2	99.543	4436
n-Heptane [1]	147.448	1.256	1460.6	431.9	113.601	4648
n-Octane [1]	163.504	1.164	1302.4	436.8	127.698	4827
n-Decane [1]	195.945	1.051	1109.6	447.0	155.750	5091
n-Dodecane [8]	228.550	0.960	987.7	445.2	184.397	5351

For a set of systems formed by the same cycloalkanol (component 1) with a series of *n*-alkanes (component 2), the relation

$$X_{12} = X_{12}^{\ddagger}\left(\frac{V_2^*}{V_2^{*\ddagger}}\right)^p \tag{1}$$

was assumed, where V_2^* is the characteristic molar volume for the *n*-alkane, and $X_{12}^{\ddagger}$ and $V_2^{*\ddagger}$ are the values of X_{12} and V_2^* for a reference system belonging to the set. In the present work, the system with *n*-hexane was used as the reference for each set, and the values of Δs_H° and $X_{12}^{\ddagger}$ were determined to fit the experimental results for V^E at cycloalkanol mole fractions x_1 of 0.5 and 0.05.

Satisfactory correlations of the excess volumes of 1-alkanol + alkane [1,2] and cycloalkanol + cycloalkane [5] mixtures were based on using a value $p = -\frac{3}{2}$ for the exponent in eqn. (1). However, preliminary calculations for the present systems indicated that X_{12} should increase more rapidly with increasing size of the *n*-alkane, and that a value $p = -\frac{1}{2}$ was more appropriate. This behavioral difference from the previous alkanol + alkane systems may be due to the greater dissimilarity of the component molecules.

TABLE 2

Model parameters for cycloalkanol + *n*-alkane systems: exchange interaction coefficient $X_{12}^{\ddagger}$ for the equation of state contribution; volume Δv_H°, enthalpy Δh_H°, and entropy Δs_H° of self-association, and equilibrium constant K (T = 298.15 K) for the association contribution

Cycloalkanol	$X_{12}^{\ddagger}$ (J cm^{-3})	Δv_H° (cm^3 mol^{-1})	Δh_H° (kJ mol^{-1})	Δs_H° (J K^{-1} mol^{-1})	K
Cyclopentanol	42.45	−10 [a]	−24.4 [a]	−25.09	568.5
Cyclohexanol	49.52	−10 [a]	−24.4 [a]	−24.83	503.3

[a] Adopted from previous work [1,2,5].

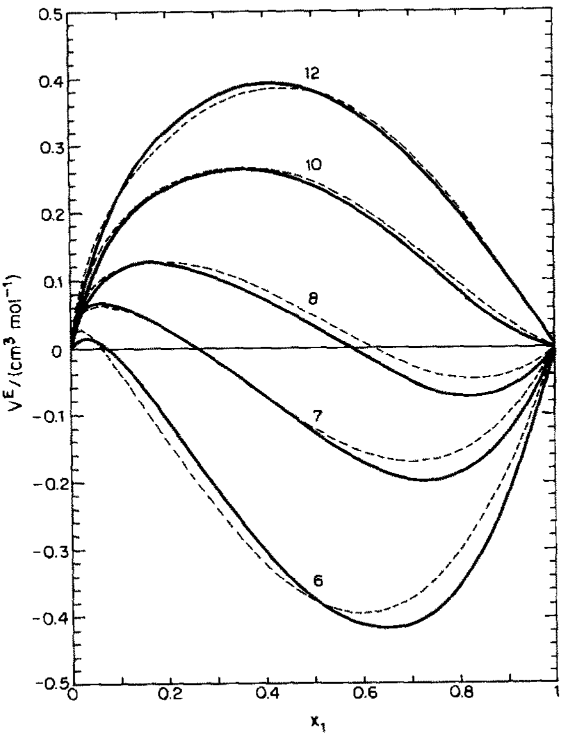

Fig. 1. Excess molar volumes V^E for binary mixtures of cyclopentanol with some *n*-alkanes C_nH_{2n+2} at 298.15 K vs. mole fraction x_1 of cyclopentanol. Curves: ———, smoothed experimental results [6,7]; — — —, calculated from present theory. Curves are labelled with the value of *n*.

Thus, the formation of the present systems involves the mixing of molecules with cyclic and chain structures, and may lead to differences in the disruption of the cycloalkanol liquid structure (non-specific and H-bond interactions), as well as in packing effects and interstitial accommodation.

The values of the model parameters Δs_H° and $X_{12}^\ddagger$, obtained from fitting the reference systems formed by each cycloalkanol with *n*-hexane, are given in Table 2. Also listed are the corresponding values of the classical equilibrium constant *K* for the association contribution at 298.15 K.

Excess molar volumes estimated for cycloalkanol + *n*-alkane systems, using the parameters obtained from the *n*-hexane reference system, are plotted in Figs. 1 and 2, where smoothed representations of the experimental results are shown for comparison. The model adequately expresses the concentration dependence of V^E and its progressive change as the number of carbon atoms in the alkane chain is increased.

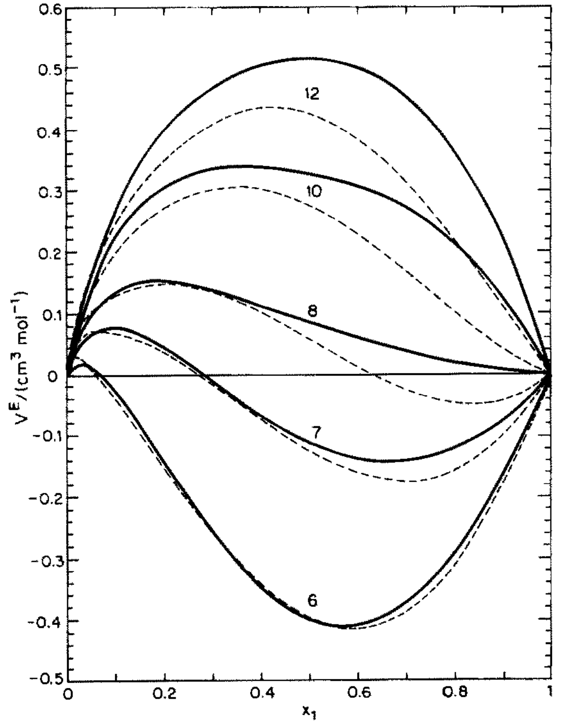

Fig. 2. Excess molar volumes V^E for binary mixtures of cyclohexanol with some *n*-alkanes C_nH_{2n+2} at 298.15 K vs. mole fraction x_1 of cyclohexanol. Curves: ———, smoothed experimental results [7]; — — —, calculated from present theory. Curves are labelled with the value of *n*.

ACKNOWLEDGEMENT

The authors are indebted to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support of this work.

REFERENCES

1 A.J. Treszczanowicz and G.C. Benson, Fluid Phase Equilibria, 23 (1985) 117.
2 A.J. Treszczanowicz and G.C. Benson, Fluid Phase Equilibria, 41 (1988) 31.
3 A.J. Treszczanowicz, D. Patterson, G.C. Benson and T. Kasprzycka-Guttman, Fluid Phase Equilibria, 50 (1989) 235.
4 A.J. Treszczanowicz, G.C. Benson and T. Kasprzycka-Guttman, Fluid Phase Equilibria, 62 (1991) 259.
5 A.J. Treszczanowicz and G.C. Benson, Thermochim. Acta, 179 (1991) 39.
6 A.J. Treszczanowicz and G.C. Benson, J. Chem. Thermodyn., 17 (1985) 123.
7 H. Kaur, J.R. Khurma and B.S. Mahl, Fluid Phase Equilibria, 45 (1989) 121.
8 G.C. Benson, C.J. Halpin and M.K. Kumaran, J. Chem. Thermodyn., 18 (1986) 1147.