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EXCESS VOLUMES OF CYCLOALKANOL + CYCLOALKANE BINARY SYSTEMS IN TERMS OF AN ASSOCIATED SOLUTION THEORY WITH A FLORY EQUATION OF STATE CONTRIBUTION

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ABSTRACT

Data for the excess volumes of binary systems formed by a cycloalkanol (C_5–C_7) with cycloalkanes (C_5–C_8) are used to examine a model in which a chemical contribution obtained from a Mecke–Kempter type of association is combined with a physical term derived from the Flory equation of state. The model provides a fairly good description of the excess volumes for the class of systems considered.

INTRODUCTION

In our previous papers, we presented a model for interpreting and correlating the excess volumes of mixtures formed from a self-associated component and an inert solvent. The treatment was applied to mixtures of 1-alkanols with *n*-alkanes [1] and with branched chain alkanes [2]. More recently, binary mixtures formed from pyridine bases with *n*-alkanes [3,4] were considered. In the present paper, we investigate the further application of the model to cycloalkanol + cycloalkane systems, using as a basis for the analysis the experimental excess volumes reported by Benson and coworkers [5–8].

THEORY

The notation and relations are the same as used in our previous publications [1,2] where derivation of the model is described. Only the formulae needed for the present application are summarized here. The excess molar volume is expressed as a sum of physical and chemical contributions

$$V^E = V^E_{phys} + V^E_{chem} \tag{1}$$

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The physical contribution, described by the Flory theory, is

$$V^{E}_{\mathrm{phys}} = (x_1V_1^* + x_2V_2^*)[\tilde{v} - (\tilde{v}_1\phi_1 + \tilde{v}_2\phi_2)] \tag{2}$$

where x_i, V_i^*, $\tilde{v}_i$ and ϕ_i are respectively the mole fraction, characteristic molar volume, reduced volume and segment fraction for component i (1 for cycloalkanol and 2 for cycloalkane); $\tilde{v}$ is the reduced volume of the mixture and is obtained from the Flory equation of state. The segment fraction is defined by

$$\phi_i = r_ix_i/(r_1x_1 + r_2x_2) \tag{3}$$

where the number of segments in a molecule of i is

$$r_i = V_i^*/17.10 \tag{4}$$

and the van der Waals volume of methane is used as a unit.

The chemical contribution to the excess molar volume, given by an athermal associated model of the Mecke–Kempter type is

$$V^{E}_{\mathrm{chem}} = \Delta v^{\ominus}_{\mathrm{H}}x_1(1/\chi_1^{\ominus} - 1/\chi_1) \tag{5}$$

where $\Delta v^{\ominus}_{\mathrm{H}}$ is the molar volume of association

$$\chi_1 = K\phi_1/\ln(1 + K\phi_1) \tag{6}$$

is the average degree of self-association in the mixture and $\chi_1^{\ominus}$ is the corresponding value for the pure component, obtained by putting $\phi_1 = 1$ in eqn. (6). The classical association constant K is eK_t, where K_t is the thermodynamic association constant given by

$$K_t = \exp[-(\Delta h^{\ominus}_{\mathrm{H}} - T\Delta s^{\ominus}_{\mathrm{H}})/RT]/r_1 \tag{7}$$

where $\Delta h^{\ominus}_{\mathrm{H}}$ and $\Delta s^{\ominus}_{\mathrm{H}}$ are the molar enthalpy and entropy of H-bond formation.

The characteristic parameters (pressure, p^*, molar value, V^* and temperature, T^*) needed to evaluate the Flory equation of state contribution, were calculated as previously [1,2] from the properties of the pure components (molar volume, $V^{\ominus}$, isobaric thermal expansivity, $\alpha_{\mathrm{p}}^{\ominus}$, and isothermal compressibility, $\kappa_{\mathrm{T}}^{\ominus}$) of the pure components. The primary data [9–15] and resulting characteristic parameters are summarized in Table 1. The Flory exchange interaction parameters, X_{12}, for a set of systems formed by the same cycloalkanol with different cycloalkanes were assumed to be proportional to $(V_2^*)^{-3/2}$, as proposed for 1-alkanol + n-alkane mixtures by Treszczanowicz and Benson [1]. For such a set of systems

$$X_{12} = X_{12}^{\ddagger}(V_2^*/V_2^{*\ddagger})^{-3/2} \tag{8}$$

where $X_{12}^{\ddagger}$ and $V_2^{*\ddagger}$ are the values of X_{12} and V_2^* for a reference system belonging to the set. Thus, application of the model to a set of systems

TABLE 1

Molar volume, $V^{\ominus}$, isobaric thermal expansivity, $\alpha_p^{\ominus}$, and isothermal compressibility, $\kappa_T^{\ominus}$, for the component liquids at 298.15 K, and characteristic values of pressure, p^*, molar volume, V^*, and temperature, T^*, obtained from the Flory formalism

Component	$V^{\ominus}$ (cm^3 mol^{-1})	$\alpha_p^{\ominus}$ (kK^{-1})	$\kappa_T^{\ominus}$ (TPa^{-1})	p^* (J cm^{-3})	V^* (cm^3 mol^{-1})	T^* (K)
Cyclopentanol	91.342 [a]	0.829 [a]	620.0 [b]	585.2	75.392	5829
Cyclohexanol	105.977 [c]	0.804 [c]	590.7 [c]	590.3	87.868	5939
Cycloheptanol	119.588 [d]	0.833 [e]	563.5 [f]	648.0	98.635	5812
Cyclopentane	94.718 [g]	1.347 [g]	1358 [g]	511.2	72.041	4496
Cyclohexane	108.751 [g]	1.220 [g]	1140 [g]	532.0	84.229	4715
Cycloheptane	121.688 [h]	1.070 [h]	923 [i]	550.5	96.434	5043
Cyclo-octane	134.827 [h]	0.982 [h]	796 [i]	568.9	108.382	5284

[a] Estimated from ref. 9. [b] Estimated from isentropic compressibility from ref. 10. [c] Ref. 11. [d] Ref. 12. [e] Determined in our laboratory. [f] Estimated from isentropic compressibility from ref. 12. [g] Ref. 13. [h] Ref. 14. [i] Estimated by the method given in ref. 15.

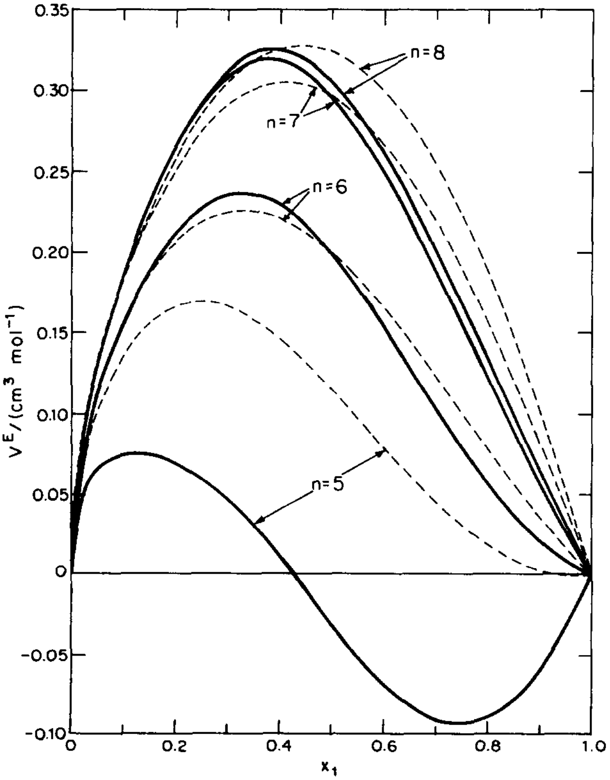

Fig. 1. Excess molar volumes, V^E, for binary mixtures of cyclopentanol with some cycloalkanes, c-C_nH_{2n}, at 298.15 K vs. mole fraction, x_1, of cyclopentanol. Curves: ———, smoothed experimental results [5–7]; — — —, calculated from present theory. Curves are labelled with the value of n.

TABLE 2

Model parameters for cycloalkanol + cycloalkane systems: exchange interaction coefficient, $X_{12}^{\ddagger}$, for the equation of state contribution; volume, $\Delta v_{\mathrm{H}}^{\ominus}$, enthalpy, $\Delta h_{\mathrm{H}}^{\ominus}$, and entropy, $\Delta s_{\mathrm{H}}^{\ominus}$, of self-association, and equilibrium constant K ($T = 298.15$ K) for the association contribution

Cycloalkanol	$X_{12}^{\ddagger}$ (J cm^{-3})	$\Delta v_{\mathrm{H}}^{\ominus}$ (cm^3 mol^{-1})	$\Delta h_{\mathrm{H}}^{\ominus}$ (kJ mol^{-1})	$\Delta s_{\mathrm{H}}^{\ominus}$ (J K^{-1} mol^{-1})	K
Cyclopentanol	35.43	−10 [a]	−24.4 [a]	−27.29	436.4
Cyclohexanol	21.30	−10 [a]	−24.4 [a]	−32.01	212.1
Cycloheptanol	26.50	−10 [a]	−24.4 [a]	−29.59	252.9

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

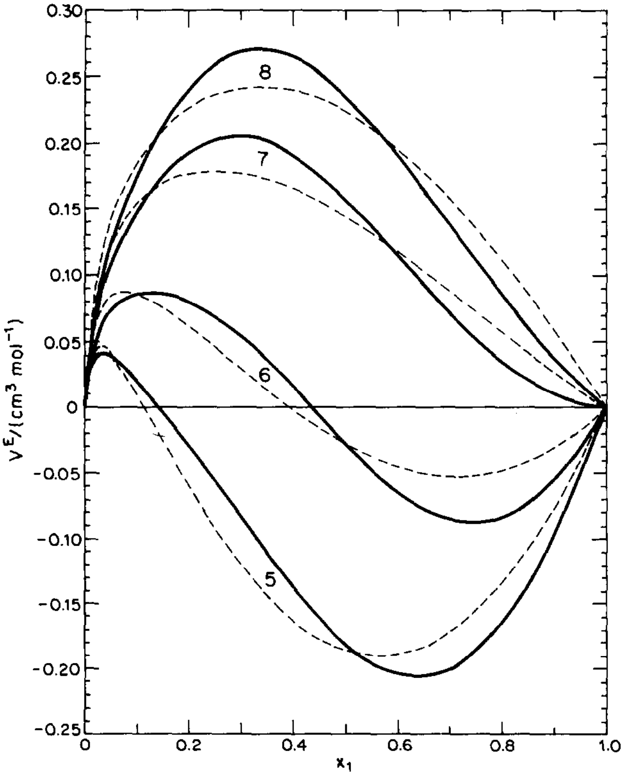

Fig. 2. Excess molar volumes, V^{E}, for binary mixtures of cyclohexanol with some cycloalkanes, c-C_nH_{2n}, at 298.15 K vs. mole fraction, x_1, of cyclohexanol. Curves: ———, smoothed experimental results [5,6,8]; — — —, calculated from present theory. Curves are labelled with the value of n.

containing a common cycloalkanol requires the values of four parameters: $X_{12}^{\ddagger}$, $\Delta v_{\mathrm{H}}^{\ominus}$, $\Delta h_{\mathrm{H}}^{\ominus}$ and $\Delta s_{\mathrm{H}}^{\ominus}$ (or K).

RESULTS AND DISCUSSION

The values of the enthalpy and volume of H-bond formation, $\Delta h_{\mathrm{H}}^{\ominus} = -24.4$ kJ mol^{-1} and $\Delta v_{\mathrm{H}}^{\ominus} = -10$ cm^3 mol^{-1}, used previously for 1-alkanol systems [1,2], were assumed in the present work. For each cycloalkanol, the system with cyclohexane was adopted as a reference, and the values of $X_{12}^{\ddagger}$ and $\Delta s_{\mathrm{H}}^{\ominus}$ (or K) were determined by the procedure used recently for pyridine base + n-alkane systems [3]. Values of the model parameters are reported in Table 2.

Curves calculated for the excess molar volumes of cycloalkanol + cycloalkane systems are plotted in Figs. 1–3, where the experimental results

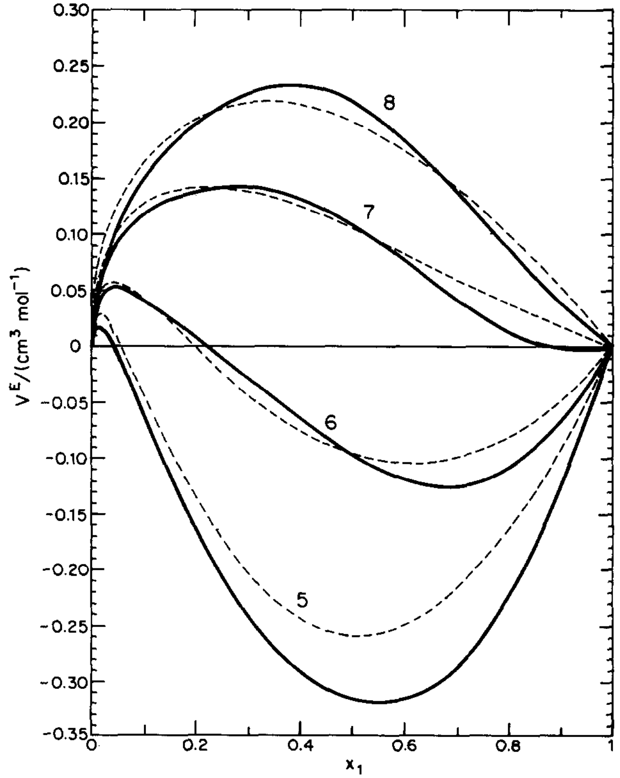

Fig. 3. Excess molar volumes, V^{E}, for binary mixtures of cycloheptanol with some cycloalkanes, c-C_nH_{2n}, at 298.15 K vs. mole fraction, x_1, of cycloheptanol. Curves: ———, smoothed experimental results [7,8]; — — —, calculated from present theory. Curves are labelled with the value of n.

are shown for comparison. The excess volume of a mixture formed from a self-associated (H-bonded) cycloalkanol and a relatively inert cycloalkane is the resultant of a number of effects which may contribute terms differing in sign. Non-specific interactions and a disruption of H-bonds make positive contributions to V^E. For the present systems, the free volume effect, which depends on differences in the characteristic pressures and temperatures of the components, makes a negative contribution (cf. Patterson and co-workers [16,17]). Packing effects or conformational changes of the molecules in the mixtures are more difficult to categorize. However, interstitial accommodation [1] and the effect of condensation [18] give further negative contributions.

An examination of Figs. 1–3 shows that from the data for one system of each set, the model predicts fairly well the concentration dependence of V^E and its progressive change as the number of carbon atoms in the cycloalkane ring is changed.

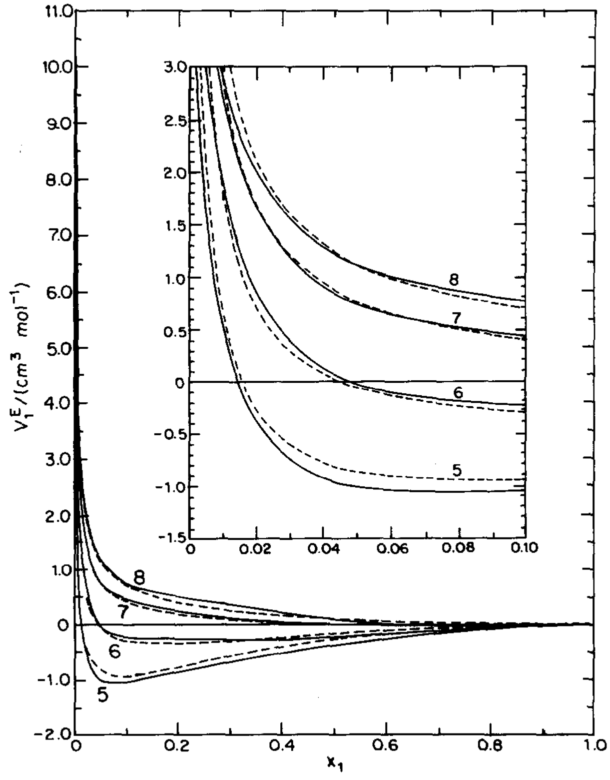

Fig. 4. Excess partial molar volumes, V_1^E, of cycloheptanol in binary mixtures with some cycloalkanes, c-C_nH_{2n}, at 298.15 K vs. mole fraction, x_1, of cycloheptanol. Curves: ———, derived from experimental results [7,8]; — — —, calculated from present theory. Curves are labelled with the value of *n*.

The greatest discrepancy between the calculated and experimental V^E curves occurs for the cyclopentanol + cyclopentane system, for which the model predicts positive values over most of the mole fraction range. In view of the agreement observed for the other systems, it is possible that this deviant behaviour may be due to one or both of the following effects: the non-specific interaction contribution predicted from the cyclohexane reference system is too high; the free volume contribution is more negative than that derived from the Flory theory, due to packing or interstitial accommodation. These effects, in the case of the cyclopentanol + cyclopentane system, may be very different from those in the other systems because of the planar structure of the cyclopentane rings of both components. The effect of the cyclopentane structure was noted by Tra [18] in considering the behaviour of binary cycloalkane systems.

It is noteworthy that the model predicts the relatively small difference observed between the V^E for mixtures of cyclopentanol with cycloheptane

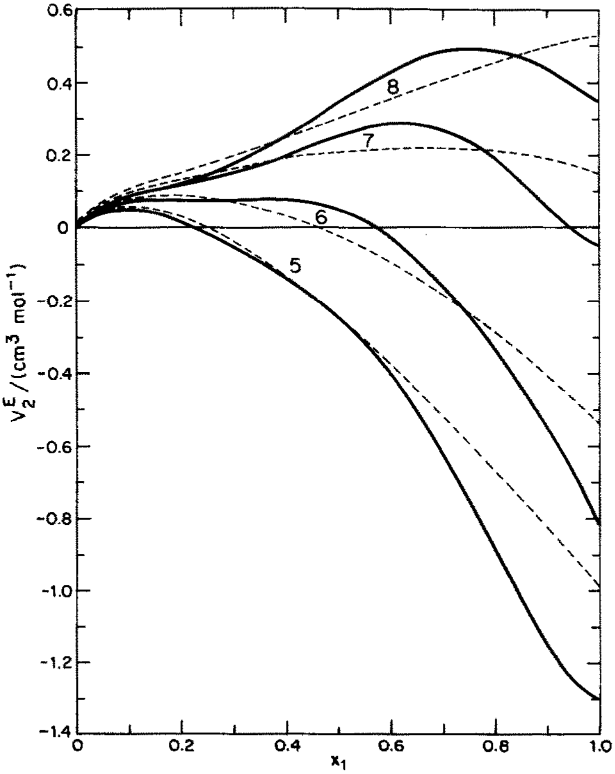

Fig. 5. Excess partial molar volumes, V_2^E, of some cycloalkanes, c-C_nH_{2n}, in binary mixtures with cycloheptanol at 298.15 K vs. mole fraction, x_1, of cycloheptanol. Curves: ———, derived from experimental results [7,8]; — — —, calculated from present theory. Curves are labelled with the value of n.

and with cyclooctane. It seems likely that the weaker size effect of cyclooctane molecules, in comparison with the smaller cycloalkanes, is attributable to a weaker correlation of molecular orientations.

Figure 4 shows the values of the excess partial molar volume, V_1^E, calculated from our model for cycloheptanol in homologous cycloalkanes, together with curves derived from the experimental data [7,8]. As found previously for 1-alkanols [1], the positive effect of the disruption of the H-bond structure usually predominates over negative effects at high dilution because, in the limit, all H-bonds are broken. However, in more concentrated solutions not all H-bonds are disrupted and negative effects may predominate. This is shown clearly for the cyclopentane and cyclohexane systems where negative minima are observed. The negative contributions decrease in absolute value with increasing size of the cycloalkane ring and V_1^E remains positive for the cyclo-octane system. The effect of free volume on the excess partial molar volumes, V_2^E, of the homologous cycloalkanes in cycloheptanol is presented in Fig. 5. For the small ring cyclopentane, the free volume effect tends to predominate and V_2^E decreases over most of the mole fraction range. This is in contrast to the large ring cyclo-octane for which V_2^E primarily increases with decreasing cyclooctane mole fraction. It can be seen from Figs. 4 and 5 that the model provides a reasonable description of the features of the excess partial molar volumes of both components.

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