ELSEVIER

Thermochimica Acta 275 (1996) 51–65

thermochimica
acta

Excess heat of mixing of 1-propanol or 2-propanol with benzene, toluene, *o*-, *m*- and *p*-xylenes at 298.15 K

K.C. Singh *, K.C. Kalra, Sanjeev Maken, Vibha Gupta

Department of Chemistry, Maharshi Dayanand University, Rohtak-124001, India

Received 27 February 1995; accepted 16 August 1995

Abstract

Excess heat of mixing data at 298.15 K for 1-propanol or 2-propanol with benzene, toluene, *o*-xylene, *m*-xylene or *p*-xylene have been reported. Analysis in terms of the Mecke–Kempter association model with a Flory contribution term and generalized quasi-lattice model by Barker is described.

Keywords: Barker quasi-lattice model; Benzene; Excess heat of mixing; Flow calorimetry; Mecke–Kempter association model; 1-Propanol; 2-Propanol; Toluene; *o*, *m* and *p*-Xylene

1. Introduction

The pronounced thermodynamic non-ideal behaviour of alkanols in non-polar solvents can best be interpreted [1–4] in terms of association of monomeric alkanol molecules into aggregates of varying degrees. Any excess thermodynamic property may be considered as made up of two parts—one corresponding to the breaking up of the hydrogen bonded network and the other resulting from the normal van der Waal's-type interactions between the alkane chain of the alcohol and the solvent. However, aromatic hydrocarbons are potential electron donors and their mixtures with alkyl halides form charge-transfer complexes due to the interactions of the π electrons of the aromatic ring and the empty 3d levels of the halogens in the alkyl halides [5–7]. Thus an additional term (which corresponds to the interaction of hydroxyl group of the alkanol with the π electrons of aromatic ring) may be required to represent the thermodynamic behaviour of alkanol–aromatic hydrocarbon mixtures.

---

* Corresponding author.

SSDI 0040-6031(95)02722-X

It has been found that the excess properties of mixtures formed from an alkanol with alkane could be correlated quite well by the association model of Mecke–Kempter-type (MK) with an added Flory contribution term [3]. The quasi-lattice theory of Barker [8] has also been used successfully to calculate the thermodynamic properties of mixing of associated solutions [9, 10].

In the present work the experimentally measured heat of mixing, H^E, of 1-propanol or 2-propanol with aromatic hydrocarbons has been interpreted in terms of the MK type of association and the quasi-lattice theory of Barker.

2. Experimental

1-Propanol, 2-propanol, benzene, toluene and *o*-, *m*- and *p*-xylenes (E. Merck) were purified by standard procedures [11]. The purities of the final samples were checked by measuring their densities at 298.15 ± 0.01 K; these agreed to within $\pm 5 \times 10^{-5}$ g cm^{-3} with the corresponding literature values [12–15]. Excess molar enthalpies, H^E, for the various binary mixtures were measured using the LKB-2107 flow microcalorimeter (LKB, Bromma, Sweden) in the manner described by Monk and Wadso [16]. The estimated uncertainties in the measured H^E values were ± 1%.

3. Results

The H^E data for the binary mixtures of 1-propanol or 2-propanol (1) with benzene, toluene, *o*-xylene, *m*-xylene or *p*-xylene (2) as a function of composition at 298.15 K are recorded in Table 1 and shown graphically in Figs. 1 and 2. The measured data were expressed by

$$H^E = x_1(1 - x_1)[A + B(2x_1 - 1) + C(2x_1 - 1)^2 + D(2x_1 - 1)^3] \quad (1)$$

where x_1 is the mole fraction of the alkanol and A, B, C and D are the adjustable parameters and evaluated by fitting Eq. (1) to $H^E/x_1(1 - x_1)$ data by the method of least squares. These parameters are recorded together with the standard deviation, σ, in Table 1.

4. Discussion

H^E data for mixtures of 1-propanol with benzene or toluene at 298.15 K have been reported in the literature [9, 12]. Our H^E values for both the systems were lower by 150 J mole^{-1} for mole fractions $0.3 < x < 0.5$. The plots of H^E vs. x_1 are skewed towards low mole fractions (x_1) of alkanols. H^E for all mixtures are positive over the whole composition range. H^E for equimolar mixtures of 1-propanol (1) with an aromatic hydrocarbon (2) vary in the order *m*-xylene ≈ *o*-xylene ≈ *p*-xylene > benzene > toluene, and for 2-propanol (1) with an aromatic hydrocarbon (2) *p*-xylene > *o*-xylene ≈ *m*-xylene > benzene > toluene.

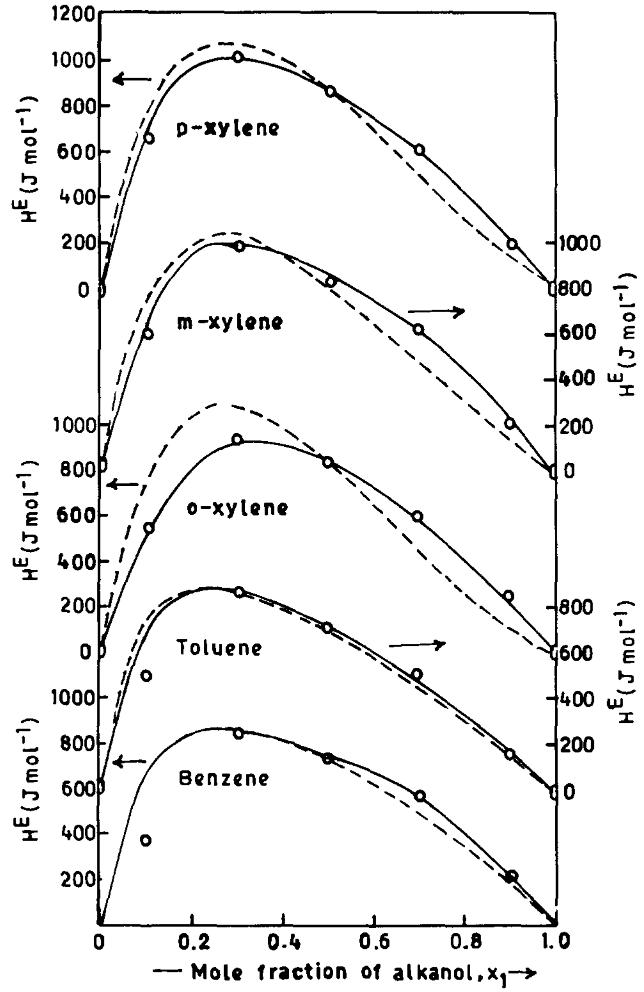

Fig. 1. Molar excess enthalpies, H^E, of 1-propanol (1)–aromatic hydrocarbon (2) at 298.15 K: —— H^E (exptl); – – – – H^E (MK model); ○ H^E (Barker's theory).

The measured H^E data may be explained qualitatively by postulating that H^E is the resultant of opposing effects. Positive values arise due to the breaking or stretching of hydrogen bonds in the self-associated alkanols, and physical dipole–dipole interactions between alkanol monomers and multimers, and also due to disruption of the favourable orientational order of aromatic hydrocarbons. Negative contributions arise from changes of "free volumes" in the real mixtures and the presence of electron donor–acceptor-type interactions between alkanols and aromatic hydrocarbons (aromatic hydrocarbons behave as electron donors). As the H^E values for all systems are highly positive over the entire range of composition, this clearly indicates that the effects contributing to the positive H^E values outweigh the effects responsible for the negative

Table 1
Molar excess enthalpies H^E, parameters A, B, C, D and standard deviation σ (/(J mol^{-1})) for various (1–2) mixtures at 298.15 K

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
1-Propanol (1)–benzene (2)					
0.0789	580	0.3453	812	0.6819	595
0.1251	742	0.3909	788	0.7458	497
0.1892	840	0.4501	758	0.8490	278
0.2561	850	0.5372	715	0.9254	106
0.2759	845	0.6099	670		
$A = 2937.27$; $B = -935.70$; $C = 2561.93$; $D = -4043.32$; $\sigma = 1.41$					
1-Propanol (1)–toluene (2)					
0.0678	530	0.3912	785	0.7216	473
0.1279	760	0.4671	725	0.8005	333
0.1974	865	0.5299	678	0.8790	175
0.2563	869	0.5811	640	0.9355	70
0.3209	835	0.6597	560		
$A = 2803.58$; $B = -1465.34$; $C = 2618.81$; $D = -3617.33$; $\sigma = 1.74$					
1-Propanol (1)–o-xylene (2)					
0.0815	452	0.3964	930	0.7278	610
0.1317	633	0.4669	917	0.8081	516
0.2093	801	0.5217	880	0.8773	342
0.2659	896	0.6029	795	0.9425	186
0.3218	912	0.6771	707		
$A = 3338.97$; $B = -2001.55$; $C = 1578.07$; $D = -129.51$; $\sigma = 1.31$					
1-Propanol (1)–m-xylene (2)					
0.0779	625	0.3917	913	0.7023	610
0.1418	815	0.4653	855	0.7667	500
0.2078	975	0.5014	825	0.8283	373
0.2861	980	0.5779	757	0.9143	175
0.3294	960	0.6418	691		
$A = 3300.99$; $B = -1661.01$; $C = 2996.50$; $D = -3123.43$; $\sigma = 1.30$					
1-Propanol (1)–p-xylene (2)					
0.1120	760	0.4773	891	0.8073	401
0.1927	968	0.5448	818	0.8595	288
0.2565	1019	0.6112	735	0.9013	195
0.3294	1009	0.6811	623	0.9667	58
0.4065	957	0.7664	483		
$A = 3469.67$; $B = -2121.20$; $C = 2458.60$; $D = -2230.37$; $\sigma = 1.87$					
2-Propanol (1)–benzene (2)					
0.0981	766	0.3942	1145	0.7427	489
0.1461	977	0.4617	1056	0.8105	331

Table 1 (*Continued*)

x_1	$H^E/(\mathrm{J\,mol^{-1}})$	x_1	$H^E/(\mathrm{J\,mol^{-1}})$	x_1	$H^E/(\mathrm{J\,mol^{-1}})$
2-Propanol (1)-benzene (2) (continued)					
0.2107	1135	0.5209	960	0.8774	186
0.2819	1201	0.6173	773	0.9327	85
0.3447	1185	0.6858	620		
$A = 3990.70$; $B = -3403.68$; $C = 1700.55$; $D = -1559.20$; $\sigma = 2.26$					
2-Propanol (1)-toluene (2)					
0.0888	662	0.4011	1166	0.7239	495
0.1627	1003	0.4727	1041	0.7990	358
0.2219	1160	0.5428	892	0.8557	267
0.2956	1236	0.6058	747	0.9026	194
0.3628	1211	0.6717	600		
$A = 3940.75$; $B = -4306.72$; $C = 1834.61$; $D = 1012.61$; $\sigma = 1.55$					
2-Propanol (1)-o-xylene (2)					
0.1213	864	0.4459	1187	0.7543	588
0.1825	1067	0.5083	1119	0.8197	395
0.2561	1198	0.5612	1041	0.8601	275
0.3143	1234	0.6229	921	0.9225	114
0.3875	1227	0.6991	738		
$A = 4520.27$; $B = -2512.74$; $C = 998.10$; $D = -2531.47$; $\sigma = 1.55$					
2-Propanol (1)-m-xylene (2)					
0.0656	675	0.3753	1222	0.7421	568
0.1213	1002	0.4694	1127	0.7994	393
0.1824	1188	0.5287	1047	0.8639	195
0.2692	1266	0.6019	918	0.9427	15
0.2938	1264	0.6775	747		
$A = 4351.56$; $B = -2752.22$; $C = 1836.81$; $D = -4346.93$; $\sigma = 2.30$					
2-Propanol (1)-p-xylene (2)					
0.1110	931	0.4334	1236	0.7224	809
0.1727	1155	0.4978	1184	0.7999	595
0.2578	1278	0.5661	1103	0.8605	403
0.3126	1290	0.6134	1031	0.9132	233
0.3719	1274	0.6883	887		
$A = 4711.82$; $B = -1994.57$; $C = 2579.72$; $D = -3398.88$; $\sigma = 1.82$					

contribution. If it is assumed that the energy associated with molecular order for all pure aromatic hydrocarbons is of the same magnitude, then the variation in H^E values for these mixtures will be due to the variations of magnitude of the specific interaction energy.

The electron-donating power of benzene is known [17] to increase with the introduction of methyl groups into the ring, as in toluene; consequently electron

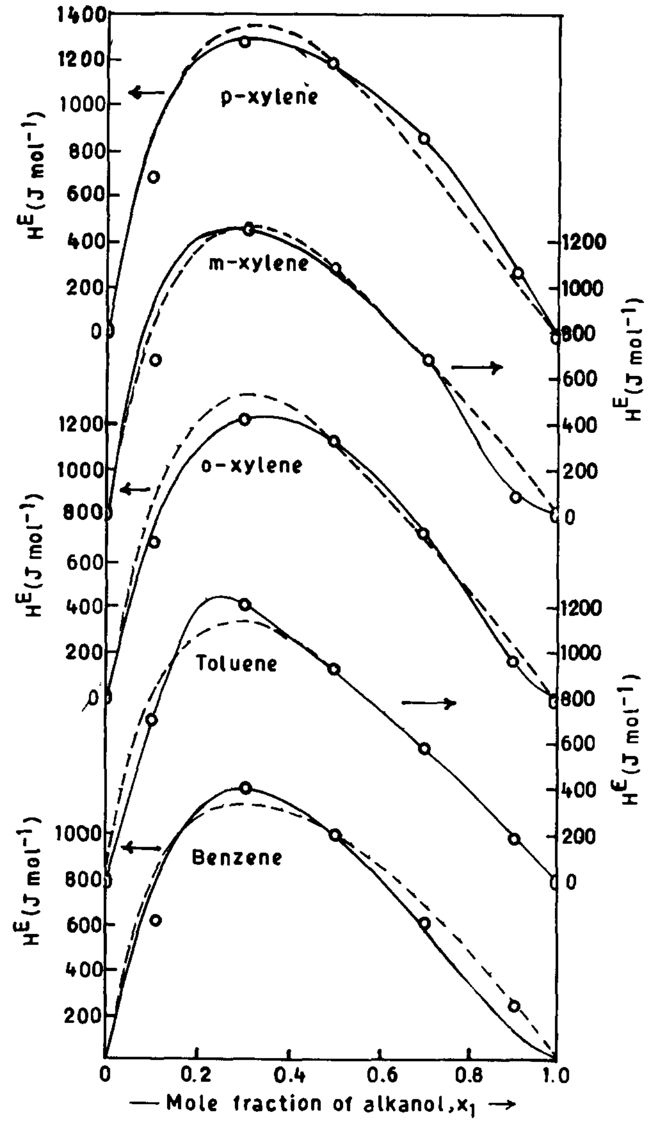

Fig. 2. Molar excess enthalpies, H^E, of 2-propanol (1)–aromatic hydrocarbon (2) at 298.15 K: ——— H^E (exptl); – – – – – H^E (MK model); ○ H^E (Barker's theory).

donor–acceptor interactions will also increase and H^E values for toluene mixtures will be less than those for benzene mixtures. This is supported by our experimental results. The introduction of two methyl groups into the benzene ring, as in xylenes, further enhances the electron-donating power of aromatic hydrocarbons; at the same time it seems that these molecules are sterically hindered by two methyl groups (which are attached to the aromatic ring) for proper orientation, which limits the interaction of the hydroxyl hydrogen of alkanol with the π electron cloud of the aromatic hydrocarbon. Thus the H^E value is slightly more positive for xylene mixtures than for those of benzene or toluene. The higher values of H^E for 2-propanol systems than those of respective 1-propanol systems suggest that the steric hindrance is greater in 2-propanol systems because of the branching in the molecule.

4.1. MK association model with Flory contribution term

This model was developed for alkanol–alkane mixtures where the alkane behaves as inert solvent [3]. It assumes that H^E and V^E are composed of a chemical term (Mecke–Kempter type association of alkanols) and a physical contribution described by Flory theory [18, 19].

$$H^E = H^E_{MK} + H^E_F \tag{2}$$

$$V^E = V^E_{MK} + V^E_F \tag{3}$$

The chemical term is

$$H^E_{MK} = \Delta h^O_H x_1 h(K^\phi, \phi_1) \tag{4}$$

$$V^E_{MK} = \Delta v^O_H x_1 h(K^\phi, \phi_1) \tag{5}$$

where

$$h(K^\phi, \phi_1) = [\phi_1 \ln(1 + K^\phi) - \ln(1 + K^\phi \phi_1)]/K^\phi \phi_1 \tag{6}$$

$$\ln K^\phi = 1 - [(\Delta h^O_H - T\Delta s^O_H)/RT] - \ln(V_1^*/17.12\,\mathrm{cm^3\,mol^{-1}}) \tag{7}$$

In these equations R is the gas constant, T is the temperature and x_1 and V_1^* are the mole fraction and hard core molar volume of the associating component. ϕ_2 and ϕ_1, $= 1 - \phi_2$, are segment volume fractions and defined by

$$\phi_2 = x_2 r_{21}/(x_1 + \gamma_{21} x_2) \tag{8}$$

where r_{21}, $= V_2^*/V_1^*$, is the size ratio parameter obtained by dividing the characteristic (hard core) molar volumes V_i^* of the components. Δv^O_H, Δh^O_H and Δs^O_H are the standard volume, enthalpy and entropy of association of alkanol.

The physical contribution is obtained from Flory theory which contains the effect of non-specific interaction between the real molecular species in the mixture, together with the free volume term. According to Flory theory [18, 19]

$$H^E_F = x_1 \theta_2 (V_1^*/\tilde{V}) X_{12} + \sum_{i=1}^{2} x_i P_i^* V_i^* [(1/\tilde{V}_i) - (1/\tilde{V})] \tag{9}$$

$$V^E_F = V^*[\tilde{V} - (\tilde{V}_1 \phi_1 + \tilde{V}_2 \phi_2)] \tag{10}$$

where X_{12} is Flory's interaction parameter and θ_2 is the contact surface fraction of component 2 and defined by

$$\theta_2 = \phi_2/(\phi_1 r_{21}^{1/3} + \phi_2) \tag{11}$$

and $V^* = (x_1 V_1^* + x_2 V_2^*)$ is the characteristic molar volume for the mixture. The reduced pressure, volume and temperature ($\tilde{P}$, $\tilde{V}$, $\tilde{T}$) are obtained by dividing pressure, volume and temperature by corresponding characteristic values (P^*, V^*, T^*) given in Table 2.

These defining relationships together with the equations

$$\tilde{V}_i^{1/3} = 1 + \alpha_i T/[3(1 + \alpha_i T)] \tag{12}$$

$$\tilde{T}_i = (\tilde{V}_i^{1/3} - 1)/\tilde{V}_i^{4/3} \tag{13}$$

and

$$P_i^* = T\alpha_i \tilde{V}_i^2 / K_{T_i} \tag{14}$$

serve to determine the characteristic and reduced quantities for the components. The isobaric expansivity and isothermal compressibility of pure component, α and K_T, respectively, (recorded in Table 2) were taken from literature [20] and K_T values for 1-propanol and 2-propanol were calculated using the following relationship [21]

$$\delta^2 = \alpha T/K_T$$

where δ the solubility parameter and was taken from the literature [22]. The reduced temperature of the mixture is given by

$$\tilde{T} = \left(\sum_{i=1}^{2} \phi_i P_i^* \tilde{T}_i\right) \Big/ \left(\sum_{i=1}^{2} \phi_i P_i^* - \phi_1 \theta_2 X_{12}\right) \tag{15}$$

and its reduced volume is obtained by solving Flory's equation of state

$$\tilde{T}\tilde{V}^{4/3} - \tilde{V}^{1/3} + 1 = 0 \tag{16}$$

4.2. Estimation of parameters of MK model

Association parameters such as $\Delta h_{\rm H}^{\rm O}$, $\Delta v_{\rm H}^{\rm O}$ and $\Delta s_{\rm H}^{\rm O}$ obtained for alkanol–alkane mixtures have the values -24.4 kJ mol^{-1}, -10 cm^3 mol^{-1} and -33 J mol^{-1}, respec-

Table 2
Molar volume (V), isobaric thermal expansivity (α) and isothermal compressibility (K_T) for the component liquids at 298.15 K; characteristic values of pressure (P^*), molar volume (V^*) and temperature (T^*) obtained from the Flory theory

Component	V/ (cm^3 mol^{-1})	$\alpha \times 10^3$/ K^{-1}	$K_T \times 10^6$/ (cm^3 J^{-1})	P^*/ (J cm^{-3})	V^*/ (cm^3 mol^{-1})	T^*/K
1-Propanol	75.164	0.9964	644.00	717.28	60.28	5239.9
2-Propanol	76.953	1.1167	795.83	676.01	60.54	4928.1
Benzene	89.399	1.217	937.78	644.45	69.27	4717.6
Toluene	106.861	1.071	1136.19	447.66	84.67	5036.3
o-Xylene	121.222	0.963	820.13	538.24	97.75	5343.2
m-Xylene	123.455	1.004	873.62	534.12	98.81	5221.5
p-Xylene	123.925	1.017	908.17	522.67	99.05	5185.2

tively. These parameters were obtained by calculating the Flory interaction parameter X_{12} from the relationship (17) and using Eqs. (10), (15) and (16)

$$V_F^E = V_{\mathrm{exptl}}^E - V_{\mathrm{MK}}^E \tag{17}$$

Here V_{MK} was initially assumed to be equal to zero. Then K^ϕ was determined by solving the equation

$$\frac{[H_{\mathrm{exptl}}^E - H_F^E]^2}{RT^2[C_{p(\mathrm{exptl})}^E - C_{p(F)}^E]} = \frac{-x_1[h(K^\phi, \phi_1)]^2}{h(K^\phi, \phi_1) + K^\phi \phi_2/(1 + K^\phi)(1 + K^\phi, \phi_1)} \tag{18}$$

provided values for H_{exptl}^E and $C_{p(\mathrm{exptl})}^E$ are available. Δh_H^O and Δs_H^O may be calculated from the relationship

$$\Delta h_H^O = (H_{\mathrm{exptl}}^E - H_F^E)/x_1 h(K^\phi, \phi_1) \tag{19}$$

and

$$\Delta s_H^O = (RT \ln K_H + \Delta h_H^O)/T \tag{20}$$

where

$$K_H = \exp[-(\Delta h_H^O - T\Delta s_H^O)/RT] \tag{21}$$

and

$$\ln K^\phi = 1 + \ln(K_H/r_1) \tag{22}$$

By assuming a constant value for Δv_H^O, V_{MK}^E was calculated from Eq. (5). Now using this V_{MK}^E value, Eq. (17) was solved again for X_{12} and the whole approximation cycle was repeated until a suitable convergence of the parameters was achieved.

Using the same values of the association parameters as obtained for alkanol–alkane mixtures [3], we calculated H^E and V^E for alkanol–aromatic hydrocarbon systems. H^E (calculated) values were found to be 50 to 60% less than experimental values and V^E (calculated) values were more absurd because in some systems even the sign was opposite to that of $V_{(\mathrm{exptl})}^E$ [23]. It has been observed by Stokes et al. [24–26] from thermodynamic, spectroscopic and dielectric measurement studies of ethanol–benzene and ethanol–p-xylene mixtures that the specific interaction between an alcohol hydroxyl group and the aromatic π electron system may be treated as a solvation of the alkanol molecules, which thus reduces the effective strength of each hydrogen bond. Therefore, it is not logical to use the same parameters for these mixtures. So we calculated the association parameters ($\Delta h_H^O, \Delta s_H^O, \Delta v_H^O$) for each system by the method described above. The $C_{p(\mathrm{exptl})}^E$ values for these systems are not available in the literature. Therefore, using $C_{p(\mathrm{exptl})}^E = 12.74\,\mathrm{J\,mol^{-1}}$ (the same value for ethanol–toluene [27]) H^E and V^E for all the systems were calculated; they are shown graphically in Figs. 1 to 4. It has been found that the calculated H^E and to some extent V^E values are in good agreement with the experimental values. Therefore, the MK model may be used successfully to represent alkanol–aromatic hydrocarbon mixtures provided new values of association parameters are used. Those indirectly take into consideration the effect of specific interactions between alkanol and aromatic hydrocarbon in the mixtures.

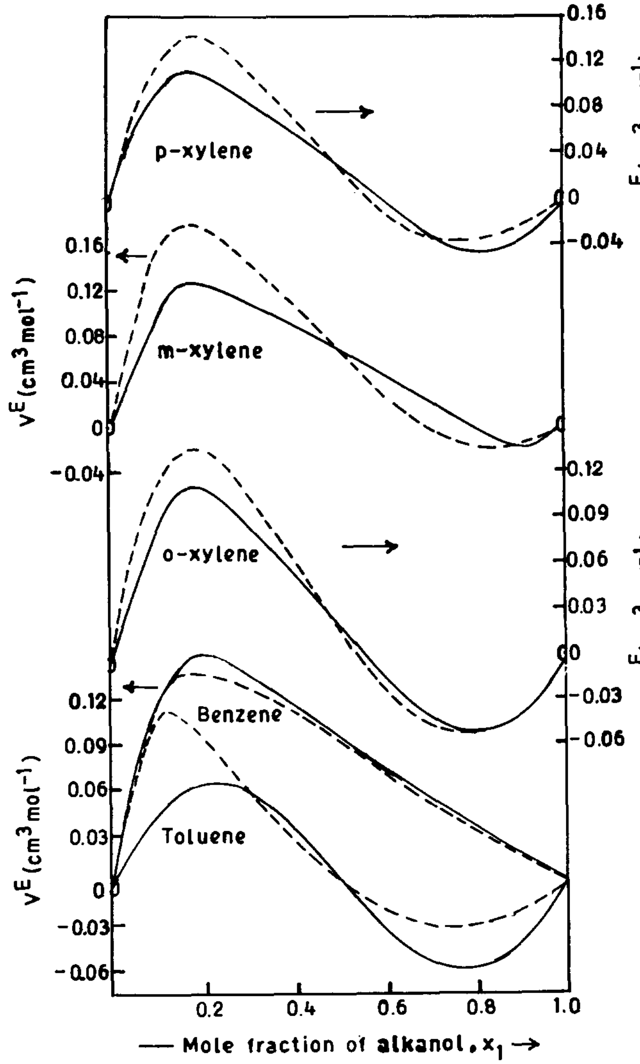

Fig. 3. Molar excess volumes, V^E, of 1-propanol (1)–aromatic hydrocarbon (2) at 298.15 K: ——— V^E (exptl); - - - - - V^E (MK model).

It can be observed from Δh_H^0 values (Table 2) that these are less than -24.4 kJ mol^{-1}, showing that the effective strength of hydrogen bonding is reduced due to the specific interaction of the alkanol with the π electrons to the aromatic hydrocarbons. The strength of the specific interaction is more for xylene systems than that for benzene or toluene systems as the values of Δh_H^0 for xylenes are less than those of benzene or toluene. The most suitable value for the molar volume of association, Δv_H^0, i.e. that which furnished H^E and V^E close to the experimental values was found to be -5 cm^3

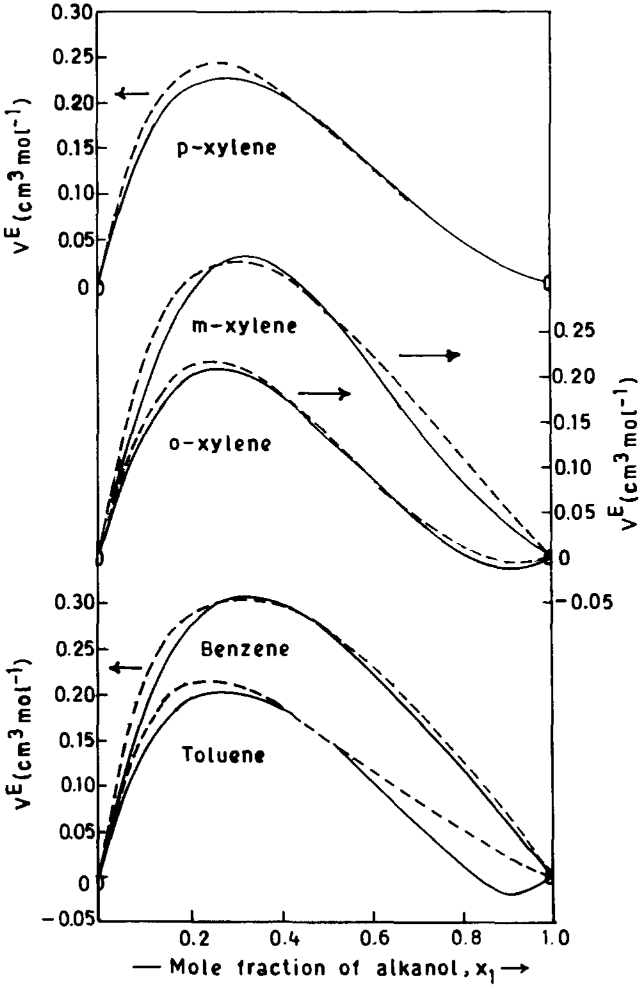

Fig. 4. Molar excess volumes, V^E, of 2-propanol (1)-aromatic hydrocarbon (2) at 298.15 K: —— V^E (exptl); – – – – V^E (MK model).

mol^{-1}. This value is less than the values -10 and $-7.5\,cm^3\,mol^{-1}$ calculated by Treszczanowicz and Benson [3] and by Stokes [28], respectively, for alkanol–alkane systems, but in agreement with the value reported by Liu et al. [29].

4.3. Generalized quasi-lattice theory

This model was developed by Barker [8] and has been applied with reasonable success to calculate the excess thermodynamic properties of associated liquids. The theory has been generalized by recognising different types of contact site on a molecule.

For the present systems, 1-propanol or 2-propanol is considered to have three types of site—hydrocarbon type (designated as type-I), hydroxyl hydrogen (H) and oxygen (O) type sites. Toluene and xylenes are considered to have two types of site—an aromatic hydrocarbon type (S) on the benzene ring and an aliphatic type (S′) on the alkyl substituent. Benzene is treated as having an S-type site only. The number of sites present on the alkanol molecules are calculated on the assumption that each carbon and each oxygen atom occupies one position in a four-fold coordinated lattice. Some of the four nearest neighbours of each carbon or oxygen atom are atoms within the same molecule. The remainder, the number of those sites available for contact with another molecule are designated by the letter Q with a superscript 1 for alkanol and 2 for the other component of the solution. The subscript to Q (H, O, I, S and S′) refers to the types of site. The number of contact sites for both the alkanols and aromatic hydrocarbons are deduced directly from the structural formulae of the compounds and are given in Table 4.

For 1-propanol or 2-propanol–benzene systems four types of site are present, resulting in the following ten interactions: H–H, H–O, H–I, H–S, O–O, O–I, O–S, I–I, I–S and S–S. The energy of interaction (U_{i-j}) of H–H, O–O, I–I and S–S sites is zero by definition. Further, the energy terms for H–I and O–I are set equal to zero; since both H and O sites may be expected to be preferentially involved in more energetic interactions (H–O, H–S and O–S), only four (H–O, H–S, O–S and I–S) interactions are considered significant. Because the energy of interaction for H–O, H–S and O–S interactions is expected to be relatively high, and number of I–S interaction is large.

For alkanol–toluene or xylene systems, one additional type of contact site (S′) is present, resulting in five additional types of interaction (H–S′, O–S′, I–S′, S–S′ and S′–S′). Since the S–S′ interaction is similar to I–S (both are aliphatic–aromatic hydrocarbon interaction), it is considered significant and the other four are set equal to zero. The interaction energy values (U_{i-j}) for different types of interaction are recorded in Table 5.

Table 3
The values of various parameters of the Mecke–Kempter model for various alkanol (1)–aromatic hydrocarbon (2) mixtures at 298.15 K

System	K^{ϕ}	X_{12}/(J cm^{-3})	Δh_H^O/(J mol^{-1})	Δs_H^O/(J K^{-1} mol^{-1})
1-Propanol–benzene	64.216	8.9504	−23930.95	−35.32
1-Propanol–toluene	38.220	−6.4079	−19887.91	−26.17
1-Propanol–*o*-xylene	10.089	−44.0099	−19024.19	−34.99
1-Propanol–*m*-xylene	14.693	−28.3810	−17807.91	−27.50
1-Propanol–*p*-xylene	12.589	−32.0774	−18102.67	−29.88
2-Propanol–benzene	23.427	6.2426	−19805.54	−30.07
2-Propanol–toluene	13.382	−20.5979	−18675.93	−31.22
2-Propanol–*o*-xylene	8.293	−38.1949	−20187.11	−40.69
2-Propanol–*m*-xylene	12.751	−18.2970	−17945.93	−29.20
2-Propanol–*p*-xylene	9.041	−30.3458	−19431.10	−37.34

Table 4
Number and types of contact sites

Compound	Type of contact site				
	Q_H^1	Q_O^1	Q_I^1	Q_S^2	$Q_{S'}^2$
1-Propanol	1	2	7	–	–
2-Propanol	1	2	7	–	–
Benzene	–	–	–	12	–
Toluene	–	–	–	11	3
o-Xylene	–	–	–	10	6
m-Xylene	–	–	–	10	6
p-Xylene	–	–	–	10	6

Table 5
The values of various interaction energies ($U_{i\,j}$) for different types of interaction for various alkanol (1)–aromatic hydrocarbon (2) mixtures at 298.15 K

System	Interaction energy/(J mol^{-1})				
	$U_{\mathrm{H\,O}}$	$U_{\mathrm{H\,S}}$	$U_{\mathrm{O\,S}}$	$U_{\mathrm{I\,S}}$	$U_{\mathrm{S\,S'}}$
1-Propanol–benzene	−24400	−5500	−100	100	
1-Propanol–toluene	−24400	−6000	−110	100	100
1-Propanol–*o*-xylene	−24400	−6400	−120	100	100
1-Propanol–*m*-xylene	−24400	−6300	−120	100	100
1-Propanol–*p*-xylene	−24400	−6600	−120	100	100
2-Propanol–benzene	−24400	−5500	−100	500	
2-Propanol–toluene	−24400	−6000	−110	500	100
2-Propanol–*o*-xylene	−24400	−6400	−120	500	100
2-Propanol–*m*-xylene	−24400	−6300	−120	500	100
2-Propanol–*p*-xylene	−24400	−6600	−120	500	100

$U_{\mathrm{H\,O}}$ is taken as −24.4 kJ mol^{-1} because the heat of association of hydrogen bond formation for alkanols (calculated by the MK model) has this value. It is found that $U_{\mathrm{H\,O}}$ is important in determining the extent of asymmetry of the heat of mixing curves. $U_{\mathrm{I\,S}}$ is adjusted independently for each system to give the correct height of each curve. As S–S′ and I–S interactions are of same nature (each is an aliphatic–aromatic interaction) for toluene and xylene mixtures $U_{\mathrm{I-S}}$ and $U_{\mathrm{S\,S'}}$ are, therefore, initially taken as of the same magnitude (100 J mol^{-1}). These values produced the correct height for 1-propanol–toluene and xylene mixtures. But for 2-propanol–toluene and xylene mixtures, $U_{\mathrm{I\,S}}$ has to be increased from 100 to 500 J mol^{-1} to give a correct height to the curve. $U_{\mathrm{H-S}}$ and $U_{\mathrm{O\,S}}$ were adjusted in such a way as to produce more refined curves. Both interactions are found to effect asymmetry, as well as the height of the heat of mixing curves to a smaller extent.

In order to calculate H^E, the following set of five quadratic equations are solved for (X) functions as given by Barker.

$$X_H[X_H + X_O\eta_{H\text{-}O} + X_I + X_S\eta_{H\text{-}S} + X_{S'}] = Q_H^1 x_1/2 \tag{23}$$

$$X_O[X_H\eta_{H\text{-}O} + X_O + X_I + X_S\eta_{O\text{-}S} + X_{S'}] = Q_O^1 x_1/2 \tag{24}$$

$$X_I[X_H + X_O + X_I + X_S\eta_{I\text{-}S} + X_{S'}] = Q_I^1 x_1/2 \tag{25}$$

$$X_S[X_H\eta_{H\text{-}S} + X_O\eta_{O\text{-}S} + X_I\eta_{I\text{-}S} + X_{S'}\eta_{S\text{-}S'}] = Q_S^2 x_2/2 \tag{26}$$

$$X_{S'}[X_H + X_O + X_I + X_S\eta_{S\text{-}S'} + X_{S'}] = Q_{S'}^2 x_2/2 \tag{27}$$

For the benzene systems Eq. (27) and the last term of the left-hand side of Eqs. (23) to (26) drop out. In the above equations component 1 is the alkanol, component 2 is the aromatic hydrocarbon, x is the mole fraction, and $\eta = \exp(-U/RT)$. All calculations were performed on a programmable calculator (Casio FX-801P). The 'X' values were so adjusted until the difference in between the R.H.S. and the L.H.S. was less than 5% of R.H.S. H^E at $x_1 = 0.1, 0.3, 0.5, 0.7$ and 0.9 were calculated for all systems from the equation

$$\begin{aligned} H^E = -2RT[&(X_O X_H - x_1 X'_O X'_H)\eta_{H\text{-}O}\ln\eta_{H\text{-}O} + X_I X_S\eta_{I\text{-}S}\ln\eta_{I\text{-}S} \\ &+ X_H X_S\eta_{H\text{-}S}\ln\eta_{H\text{-}S} + X_O X_S\eta_{O\text{-}S}\ln\eta_{O\text{-}S} + X_S X_{S'}\eta_{S\text{-}S'}\ln\eta_{S\text{-}S'}] \end{aligned} \tag{28}$$

where X'_O and X'_H are the values of the X functions at $x_1 = 1$.

The calculated values of H^E are plotted in Figs. 1 and 2. It can be observed that the calculated and experimental values agree reasonably well, except the value at $x_1 = 0.1$. As the presence of an alkyl substituent in the benzene ring enhances the electron density of the ring and will, therefore, increase the strength of H–S and O–S interactions. The values of these parameters ($U_{H\text{-}S}$ and $U_{O\text{-}S}$) that produced the best fit of the experimental data, did, in fact, follow the predicted change.

It can be concluded that the generalized quasi-lattice model is useful for interpreting heat of mixing data for alkanol–aromatic hydrocarbon systems. By assigning values to the lattice parameters that are based solely on the geometry of the molecule and making only a rough estimate of reasonable values of energy parameters, one can get qualitative information about the height and shape of H^E vs. composition curve.

Acknowledgement

SM and VG thank CSIR, New Delhi and UGC, New Delhi for financial assistance.

References

[1] F. Smith, Aust. J. Chem., 30 (1977) 43.
[2] E.E. Tucker and E.D. Becker, J. Phys. Chem., 77 (1973) 1783.
[3] A.J. Treszczanowicz and G.C. Benson, Fluid Phase Equilibria, 23 (1985) 117.
[4] K.N. Marsh and C. Burfitt, J. Chem. Thermodyn., 7 (1975) 955.

[5] K.C. Kalra, K.C. Singh, M. Soni and D.C. Spah, J. Chem. Thermodyn., 22 (1990) 771.
[6] P. Kumar, K.C. Kalra and K.C. Singh, Thermochim. Acta, 188 (1991) 151.
[7] K.C. Singh, K.C. Kalra and P. Kumar, Indian J. Chem., 29A (1990) 124.
[8] J.A. Barker, J. Chem. Phys., 20 (1952) 1526.
[9] J.R. Goates, R.L. Snow and J.B. Ott, J. Phys. Chem., 66 (1962) 1301.
[10] R.K. Nigam, P.P. Singh, M. Singh and K.C. Singh, Indian J. Chem. 19A (1980) 192.
[11] A. Vogel, A Text Book of Practical Organic Chemistry, 3rd edn, ELBS, Longmans, London, 1978.
[12] I. Brown and W. Fock, Aust. J. Chem., 14 (1961) 387.
[13] A.H. Buep and M. Baron, J. Phys. Chem., 92 (1988) 840.
[14] V.K. Sharma, P.P. Singh and S. Maken, J. Chem. Eng. Data, 39 (1994) 238.
[15] G. Tardajas, M. Diaz Pena and E. Aicart, J. Chem. Thermodyn., 18 (1986) 683.
[16] P. Monk and I. Wadso, Acta Chem. Scand., 22 (1968) 1842.
[17] R.K. Nigam and K.C. Singh, J. Chem. Soc. Faraday Trans. I, 175 (1979) 1120.
[18] P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.
[19] A. Abe and P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1838.
[20] J. Singh, H. Pflung and G.C. Benson, J. Phys. Chem., 72 (1968) 1939.
[21] J.H. Hildbrand, J.M. Prausnitz and R.L. Scott, Regular and Related Solutions, Van Nostrand Reinhold, New York, 1970.
[22] R.C. Weast, Handbook of Chemistry and Physics, 67th edn, CRC Press, Boca Raton, FL.
[23] K.C. Singh, K.C. Kalra, S. Maken and B.L. Yadav, J. Chem. Eng. Data, 39 (1994) 241.
[24] R.H. Stokes and K.N. Marsh, J. Chem. Thermodyn., 8 (1976) 709.
[25] R.H. Stokes and C.J. Burfitt, J. Chem. Thermodyn., 5 (1973) 623.
[26] R.H. Stokes and M.J. Adamson, J. Chem. Soc. Faraday Trans. I, 71 (1975) 1707.
[27] S.C.P. Hwa and W.T. Ziegler, J. Phys. Chem., 70 (1966) 2572.
[28] R.H. Stokes, J. Chem. Soc. Faraday Trans. I, 73 (1977) 1140.
[29] A. Liu, F. Kohler, L. Karrer, A. Gaube and P. Spellucci, Pure Appl. Chem., 61 (1989) 1441.