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

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Abstract

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

Keywords: Benzene; Heat of mixing; Model; Propanol; Toluene; Xylene

1. Introduction

The pronounced thermodynamic non-ideal behaviour of alkanols in non-polar solvents can best be interpreted [1–4] in terms of the association of monomeric alkanol molecules into aggregates of varying degrees. Any excess thermodynamic property may be considered as being 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 of 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 may be required (which corresponds to the interaction of the hydroxyl group of the alkanol with the π -electrons of the aromatic ring) to represent the thermodynamic behaviour of alkanol + aromatic hydrocarbon mixtures.

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It has been found that the excess properties of mixtures formed from an alkanol with an alkane can be correlated quite well by an association model of Mecke–Kempter type (MK) with an added Flory contribution term [3]. 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 an MK type of association and Barker's quasi-lattice theory.

2. Experimental

1-Propanol, 2-propanol, benzene, toluene, *o*-, *m*- and *p*-xylenes (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 an 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 are $\pm 1\%$.

3. Results

The H^E data for the binary mixtures of 1-propanol and 2-propanol (1) + benzene, + *o*-xylene, + *m*-xylene and + *p*-xylene (2) as a function of composition at 298.15 K are recorded in Table 1 and shown graphically in terms of Eq. (1) 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 alkanol and A , B , C , 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

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

The measured H^E data may be explained qualitatively by postulating that H^E is the result of opposing effects. A positive value arises from the breaking or stretching of

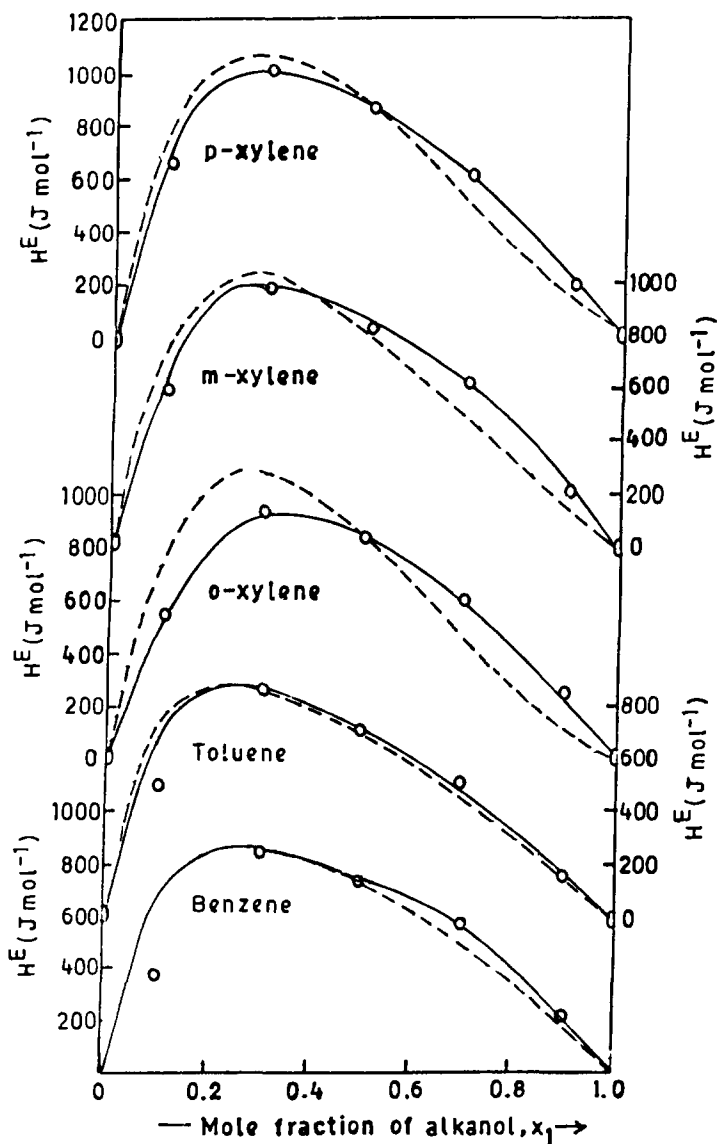


Fig. 1. Molar excess enthalpies, H^E , of 1-propanol (1) + aromatic hydrocarbon (2) at 298.15 K: — H^E (exptl); - - - H^E (MK model); O, H^E (Barker's theory).

hydrogen bonds in the self-associated alkanols, from physical dipole–dipole interactions between alkanol monomers and multimers, and also because of disruption in the favourable orientational order of aromatic hydrocarbons. Negative contributions arise from a change in free volumes in the real mixture 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

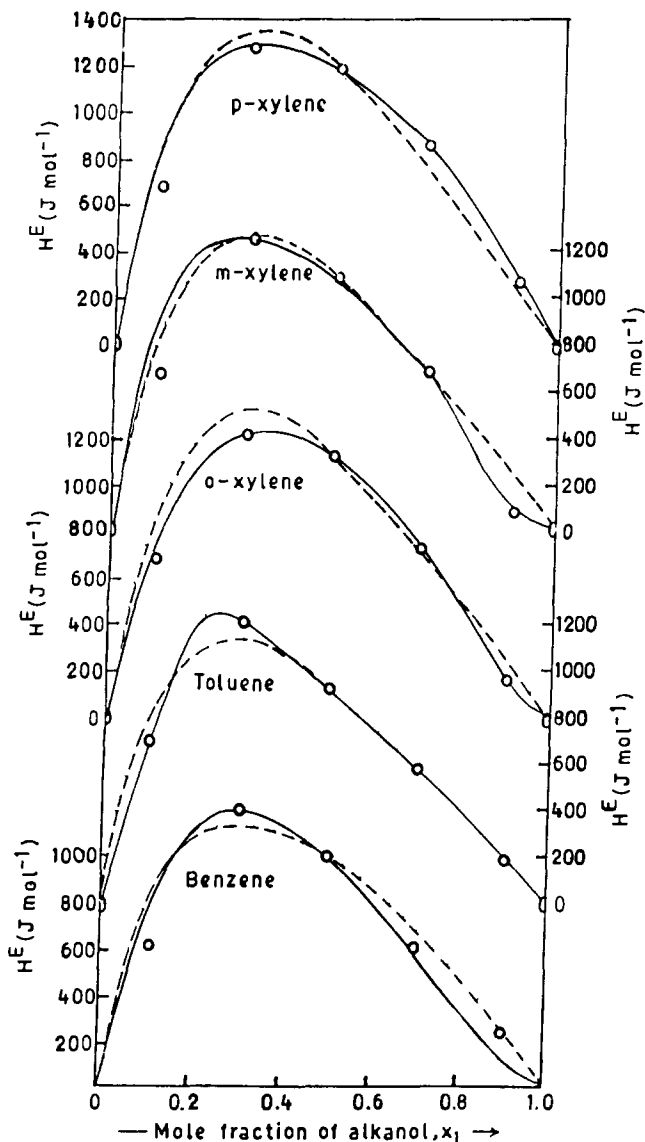


Fig. 2. Molar excess enthalpies, H^E , of 2-propanol (1) + aromatic hydrocarbon (2) at 298.15 K: — H^E (exptl); - - - H^E (MK model); O, H^E (Barker's theory).

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 negative contributions. 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 variation in magnitude of the specific interaction energy in these mixtures.

Table 1

Molar excess enthalpies H^E , parameters A, B, C, D and standard deviation σ for various (1 + 2) mixtures at 298.15 K^a

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) + <i>o</i> -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) + <i>m</i> -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) + <i>p</i> -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	0.6881	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
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

Table 1 (Continued)

x_1	$H^E(\text{J mol}^{-1})$	x_1	$H^E(\text{J mol}^{-1})$	x_1	$H^E(\text{J mol}^{-1})$
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) + <i>o</i> -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) + <i>m</i> -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) + <i>p</i> -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		
$A = 4711.82; B = -1994.57; C = 2579.72; D = -3398.88; \sigma = 1.82$					

^a A, B, C, D and σ are in J mol^{-1} .

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-donor–electron-acceptor interactions will also increase and H^E values for toluene mixtures will be less than those of 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 and, at the same time, it seems that these molecules are sterically hindered by two methyl groups (which are attached to the aromatic ring) from the proper orientation, which limits the interaction of the hydroxyl hydrogen of the alkanol with the π -electron cloud of the aromatic hydrocarbon. Thus, H^E values are slightly more positive for xylene mixtures than those of benzene or toluene. The higher values of H^E for 2-propanol systems over those of the respective 1-propanol systems, suggest that the steric hindrance is more in 2-propanol systems due to the branching of alkyl group in 2-propanol.

4.1. MK association model with Flory contribution term

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

$$H^E = H_{MK}^E + H_F^E \quad (2)$$

$$V^E = V_{MK}^E + V_F^E \quad (3)$$

The chemical term is

$$H_{MK}^E = \Delta h_H^0 x_1 h(K^\phi, \phi_1) \quad (4)$$

$$V_{MK}^E = \Delta v_H^0 x_1 h(K^\phi, \phi_1) \quad (5)$$

where

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

$$\ln K^\phi = 1 - [(\Delta h_H^0 - T \Delta s_H^0) / RT] - \ln(V_1^* / 17.12 \text{ cm}^3 \text{ mol}^{-1}) \quad (7)$$

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. In the next equation, ϕ_2 and $\phi_1 = 1 - \phi_2$ are segment volume fractions and defined by

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

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_H^0 , Δh_H^0 and Δs_H^0 are the standard volume, enthalpy and entropy of association of alkanol.

The physical contribution is obtained from Flory's 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 the Flory theory [18,19]

$$H_F^E = x_1 \theta_2 (V_1^* / \tilde{V}_i) \chi_{12} + \sum_{i=1}^2 x_i P_i^* V_i^* [(1/\tilde{V}_i) - (1/\tilde{V})] \quad (9)$$

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

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

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

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 the corresponding characteristic values (P^* , V^* , T^*) given in Table 2.

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	$V/$ ($\text{cm}^3 \text{mol}^{-1}$)	$\alpha \times 10^3$ (K^{-1})	$K_T \times 10^6$ ($\text{cm}^3 \text{J}^{-1}$)	$P^*/$ (J cm^{-3})	$V^*/$ ($\text{cm}^3 \text{mol}^{-1}$)	$T^*/$ (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
<i>o</i> -Xylene	121.222	0.963	820.13	538.24	97.75	5343.2
<i>m</i> -Xylene	123.455	1.004	873.62	534.12	98.81	5221.5
<i>p</i> -Xylene	123.925	1.017	908.17	522.67	99.05	5185.2

These defining relations together with the equations

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

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

and

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

serve to determine the characteristic and reduced quantities for the components; α and K_T are the isobaric expansivity and isothermal compressibility of the pure components (recorded in Table 2) and were taken from the literature [20]; the K_T values for 1-propanol and 2-propanol were evaluated with the following relation [21]

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

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

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

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

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

4.2. Estimation of the MK model parameters

The association parameters Δh_{H}^0 , Δv_{H}^0 and Δs_{H}^0 obtained for alkanol + alkane mixtures have the values $-24.4 \text{ kJ mol}^{-1}$, $-10 \text{ cm}^3 \text{mol}^{-1}$ and -33 J mol^{-1} respectively. These parameters were obtained by calculating the Flory interaction parameter χ_{12} from relation (17) and using Eqs. (10), (13) and (15)

$$V_{\text{F}}^{\text{E}} = V_{\text{exptl}}^{\text{E}} - V_{\text{MK}}^{\text{E}} \quad (17)$$

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

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

Provided values for $H_{\text{exptl}}^{\text{E}}$ and $C_{\text{P(exptl)}}^{\text{E}}$ are available, $\Delta h_{\text{H}}^{\circ}$ and $\Delta s_{\text{H}}^{\circ}$ may be calculated from the relation

$$\Delta h_{\text{H}}^{\circ} = (H_{\text{exptl}}^{\text{E}} - H_{\text{F}}^{\text{E}}) / x_1 [h(K^{\phi}, \phi_1)] \quad (19)$$

and

$$\Delta s_{\text{H}}^{\circ} = (RT \ln K_{\text{H}} + \Delta h_{\text{H}}^{\circ}) / T \quad (20)$$

where

$$K_{\text{H}} = \exp [-(\Delta h_{\text{H}}^{\circ} - T \Delta s_{\text{H}}^{\circ}) / RT] \quad (21)$$

and

$$\ln K^{\phi} = 1 + \ln (K_{\text{H}} / r_1) \quad (22)$$

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

Using the same values of association parameters as obtained for alkanol + alkane mixtures [3], we calculated the H^{E} and V^{E} for alkanol + aromatic hydrocarbon systems. H^{E} (calculated) values were found to be 50–60% less than experimental values and V^{E} (calculated) values were more unrealistic because in some systems even the sign was opposite to the V^{E} (exptl) [23]. It has been observed by Stoke and coworkers [24–26] from thermodynamic, spectroscopic and dielectric measurements studies of ethanol + benzene and + *p*-xylene mixtures that the specific interaction between alcoholic hydroxyl groups and the aromatic π -electron system may be treated as a solvation of the alkanol molecules thus reducing 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 ($\Delta h_{\text{H}}^{\circ}$, $\Delta s_{\text{H}}^{\circ}$, $\Delta v_{\text{H}}^{\circ}$) for each system by the method described above. The $C_{\text{P(exptl)}}^{\text{E}}$ values for these systems are not available in the literature. Therefore, using $C_{\text{P(exptl)}}^{\text{E}} = 12.74 \text{ J mol}^{-1}$ (the same value as for ethanol + toluene [26]) H^{E} and V^{E} for all the systems were calculated and are shown graphically in Figs. 1–4. It has been found that the calculated H^{E} and to some extent the 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 the association parameters are used. These indirectly take into consideration the effect of specific interactions in alkanol + aromatic hydrocarbon mixtures.

It can be observed from $\Delta h_{\text{H}}^{\circ}$ values (Table 3) that these are less than $-24.4 \text{ kJ mol}^{-1}$, showing that the effective strength of H-bonding is reduced due to the specific interaction between alkanol and the π -electrons of aromatic hydrocarbons. The

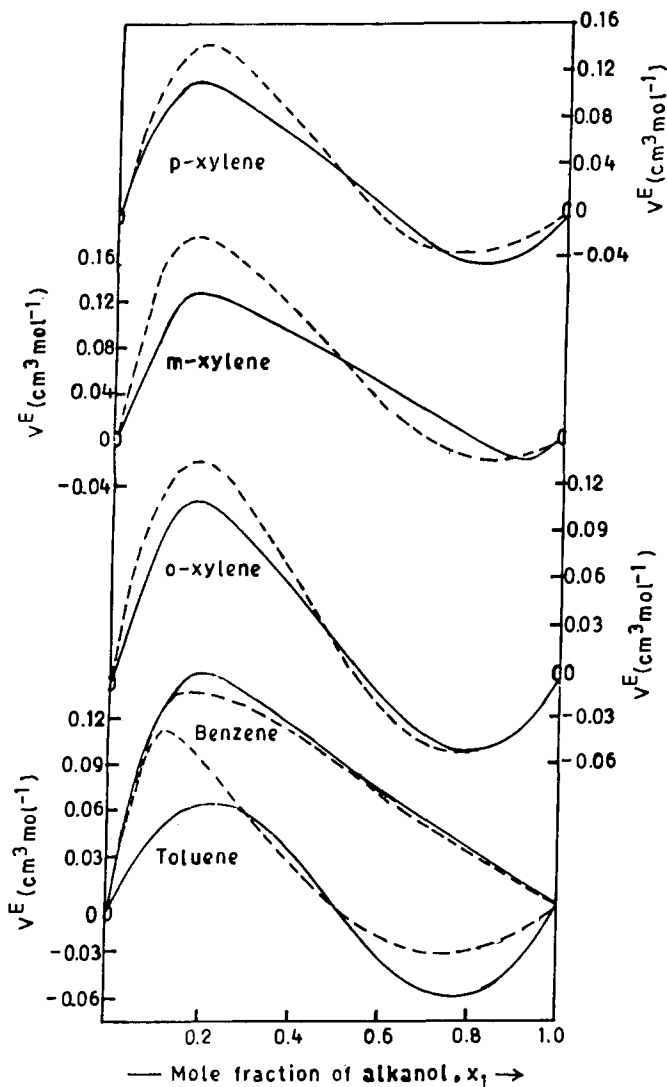


Fig. 3. Molar excess volumes, V^E , of 1-propanol(1) + aromatic hydrocarbon(2) at 298.15 K: — $V^E(\text{exptl})$; - - - $V^E(\text{MK model})$.

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 that reproduced H^E and V^E close to the experimental values is found to be $-5 \text{ cm}^3 \text{mol}^{-1}$. This value is less than the values $-10 \text{ cm}^3 \text{mol}^{-1}$ and $-7.5 \text{ cm}^3 \text{mol}^{-1}$ calculated by Trenzczanowicz and Benson [3] and Stokes [28] respectively for alkanol + alkane systems, but is in agreement with the value reported by Liu et al. [29].

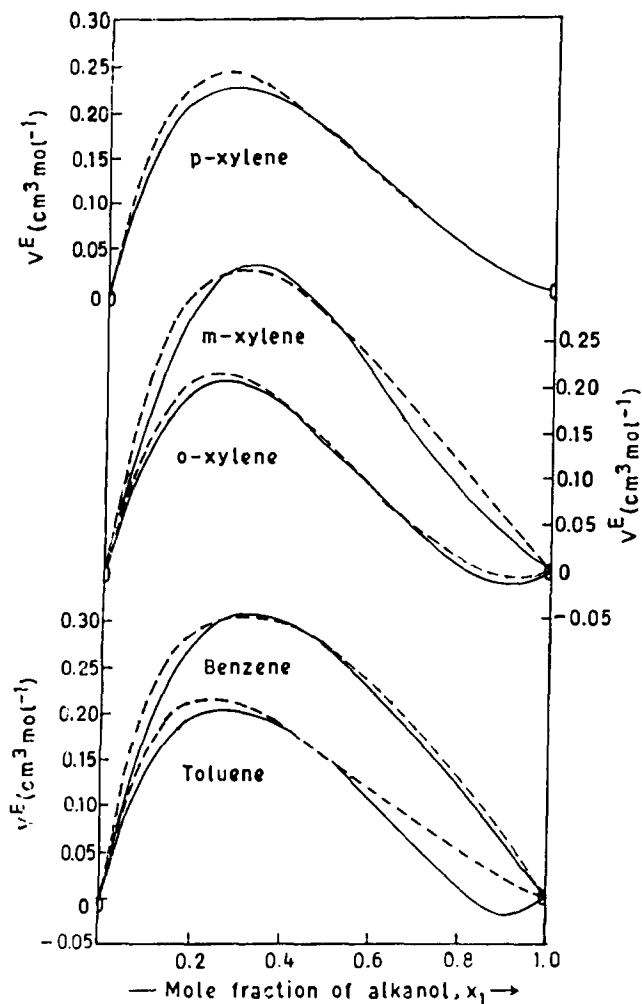


Fig. 4. Molar excess volumes, V^E , of 2-propanol(1) + aromatic hydrocarbon(2) at 298.15 K: — V^E (exptl); - - - V^E (MK model).

4.3. Generalized quasi-lattice theory

This model was developed by Barker [8] and has been applied with reasonable success to calculation of the excess thermodynamic properties of associated liquids. The theory has been generalized by recognising different types of contact sites on a molecule. For the present systems, 1-propanol or 2-propanol is considered to have three types of sites: hydrocarbon type (designated as type I), hydroxyl hydrogen (H), and oxygen (O) type sites. Toluene and xylenes are considered to have two types of sites: an aromatic hydrocarbon type (S) on the benzene ring and an aliphatic type (S') on the

Table 3

The values of various parameters of the Mecke–Kempter model for various alkanols (1) + aromatic hydrocarbons (2) at 298.15 K

System	K^ϕ	χ_{12} (J cm^{-3})	Δh_{H}^0 (J mol^{-1})	Δs_{H}^0 ($\text{J K}^{-1} \text{mol}^{-1}$)
1-Propanol + benzene	64.216	8.9504	− 23930.95	− 35.32
1-Propanol + toluene	38.220	− 6.4079	− 19887.91	− 26.17
1-Propanol + <i>o</i> -xylene	10.089	− 44.0099	− 19024.19	− 34.99
1-Propanol + <i>m</i> -xylene	14.693	− 28.3810	− 17807.91	− 27.50
1-Propanol + <i>p</i> -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 + <i>o</i> -xylene	8.293	− 38.1949	− 20187.11	− 40.69
2-Propanol + <i>m</i> -xylene	12.751	− 18.2970	− 17945.93	− 29.20
2-Propanol + <i>p</i> -xylene	9.041	− 30.3458	− 19431.10	− 37.34

alkyl substituent. Benzene is treated as having only an S-type site. 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. Subscripts to Q (H, O, I, S and S') refer to the type of sites. 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 the 1-propanol or 2-propanol + benzene systems, four types of sites 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. 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

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
<i>o</i> -Xylene	–	–	–	10	6
<i>m</i> -Xylene	–	–	–	10	6
<i>p</i> -Xylene	–	–	–	10	6

(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 the number of I–S interactions is large.

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

The U_{H-O} is taken as $-24.4 \text{ kJ mol}^{-1}$ because the heat of association of hydrogen bond formation for alkanols (calculated by the MK model) has this value. It is found that U_{H-O} is important in determining the extent of asymmetry of the heat of mixing curves. The U_{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 and aromatic interaction), therefore, for toluene and xylenes mixtures U_{I-S} and $U_{S-S'}$ are initially taken as having the same magnitude (100 J mol^{-1}). These values produced the correct height for 1-propanol + toluene and + xylenes mixtures. But for 2-propanol + toluene and + xylene mixtures, U_{I-S} has to increase from 100 J mol^{-1} to 500 J mol^{-1} to give the correct height to the curve. U_{H-S} and U_{O-S} were adjusted in such a way as to produce more refined curves. Both interactions are found to affect the 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 were solved for (X) functions as given by Barker

$$X_H[X_H + X_O\eta_{H-O} + X_I + X_S\eta_{H-S} + X_S] = Q_H^1 x_1/2 \quad (23)$$

$$X_O[X_H\eta_{H-O} + X_O + X_I + X_S\eta_{O-S} + X_S] = Q_O^1 x_1/2 \quad (24)$$

$$X_I[X_H + X_O + X_I + X_S\eta_{I-S} + X_S] = Q_I^1 x_1/2 \quad (25)$$

Table 5

The values of various interaction energies (U_{i-j}) for different types of interactions for various alkanols (1) + aromatic hydrocarbons (2) at 298.15 K

System	Interaction energy/(J mol ⁻¹)				
	U_{H-O}	U_{H-S}	U_{O-S}	U_{I-S}	$U_{S-S'}$
1-Propanol + benzene	-24400	-5500	-100	100	-
1-Propanol + toluene	-24400	-6000	-110	100	100
1-Propanol + <i>o</i> -xylene	-24400	-6400	-120	100	100
1-Propanol + <i>m</i> -xylene	-24400	-6300	-120	100	100
1-Propanol + <i>p</i> -xylene	-24400	-6600	-120	100	100
2-Propanol + benzene	-24400	-5500	-100	500	-
2-Propanol + toluene	-24400	-6000	-110	500	100
2-Propanol + <i>o</i> -xylene	-24400	-6400	-120	500	100
2-Propanol + <i>m</i> -xylene	-24400	-6300	-120	500	100
2-Propanol + <i>p</i> -xylene	-24400	-6600	-120	500	100

$$X_S [X_H \eta_{H-S} + X_O \eta_{O-S} + X_I \eta_{I-S} + X_S \eta_{S-S}] = Q_S^2 x_2/2 \quad (26)$$

$$X_S [X_H + X_O + X_I + X_S \eta_{S-S} + X_S] = Q_S^2 x_2/2 \quad (27)$$

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

$$H^E = -2RT [(X_O X_H - x_1 X'_O X'_H) \eta_{H-O} \ln \eta_{H-O} + X_I X_S \eta_{I-S} \ln \eta_{I-S} + X_H X_S \eta_{H-S} \ln \eta_{H-S} + X_O X_S \eta_{O-S} \ln \eta_{O-S} + X_S X_S \eta_{S-S} \ln \eta_{S-S}] \quad (28)$$

where X'_O and X'_H are the values of 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 $x_1 = 0.1$. 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-S} and U_{O-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 rough estimates of reasonable values for the energy parameters, one can get qualitative information about the height and shape of the H^E vs. composition curve.

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