Thermodynamics of binary mixtures of alkylbenzenes: Role of orientational order in benzene + alkylbenzene mixtures

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Abstract

The results of measurements for excess molar enthalpies, excess molar heat capacities and excess molar volumes of a number of mixtures consisting of alkylbenzenes reported from our laboratories and the literature data on similar systems have been examined here. It has been noted that the behavoiur of mixtures containing benzene + alkylbenzene is quite different from those mixtures in which both the components are alkylbenzenes. These observations have been explained in terms of importance of orientational order present in pure benzene. In general the excess functions depend on the difference (n_2 - n_1) in the chain lengths of alkyl groups of the two components.

INTRODUCTION

In recent years short range orientational order contribution to excess thermodynamic properties has been shown to be of importance in certain category of mixtures. This contribution is considered to be associated with the effect of order which may be decreased or increased in passing from components in pure state into their mixture (ref. 1). Flory et al (ref. 2) in their paper had concluded that large positive contribution to excess entropy in certain mixtures was due to ordered structure of the components. Patterson et al have made important contributions in understanding the nature of orientational order in pure alkanes and in understanding the effect of orientational order on excess thermodynamic properties. Various studies (ref. 3,6) indicate that order in n-alkanes decreases with increase in temperature. In thermodynamic sense, existence of order apparently lowers enthalpy, volume and entropy of a liquid and since order decreases with increase of temperature, heat capacity is enhanced. When an ordered liquid is mixed with a quasi- spherical molecule such as 2,2-dimethylbutane or cyclohexane or carbontetrachloride there is net decrease in order (ref. 3,7) and this loss of order during mixing gives positive contributions to excess molar enthalpy, excess molar volume, and excess molar entropy and negative contribution to excess molar heat capacity. Non-thermodynamic studies, e.g., depolarised Rayleigh scattering studies (ref. 8) also support the existence of order correlations in some liquids in agreement with X-ray diffraction studies (ref. 9).

Grolier, Wilhelm and coworkers have studied (ref. 10-15) the thermodynamics of mixtures of the type A + n-alkane (where A is 1,2,4-trimethylbenzene or chlorobenzene or dichlorobenzene or 1-chloronephathelene). For these systems excess molar enthalpy decreases as n increases and excess molar heat capacity in some cases is greater than zero. This behaviour has been explained by suggesting that order of some sort is being created in these mixtures. Grolier et al (ref. 11-14), Wilhelm (ref. 10) and Inglese et al (ref. 15) suggest that this order is associated with a change in the trans gauche population of n-alkane favoured by interaction between the trans conformers and the flat molecule while others (ref. 16,17) have suggested that ordering is due to restriction of n-alkane segmental rotational motion by plate-shaped molecules.

We have recently reported excess molar enthalpies, excess molar heat capacities and excess molar volumes for a number of binary mixtures containing benzene (or alkylbenzene) and another alkylbenzene (ref. 18-24). Benson and coworkers (ref. 25-27) and Woycicki and Sadowska (ref.28) and Woycicki (ref. 29) have also re ported excess molar enthalpy and excess molar heat capacity for a number of similar systems. In this paper we shall discuss the thermodynamics of these mixtures in the light of orientational order in pure benzene.

EXPERIMENTAL

For determination of excess molar enthalpy a flow microcalorimeter (LKB-Bio Activity Monitor) was used. A general description of the instrument is given by Monk and Wadso (ref. 30) and Suurkuush and Wadso (ref. 31). The calorimeter was calibrated using known excess molar enthalpies of (benzene + tetrachloromethane and benzene + cyclohexane) at 298.15 K (ref. 32). The functioning of the calorimeter was tested by determining excess molar enthalpy at 298.15 K for benzene + methylbenzene (ref. 25) benzene + ethylbenzene (ref. 26) and cyclohexane + hexane (ref. 33) and comparing experimental results with literature values. The experimental results agree with literature values within 1.1 per cent over the entire mole fraction range. Excess molar heat capacities for some of the mixtures were calculated from temperature dependence of excess molar enthalpies.

Excess molar volumes of the alkylbenzene mixtures were calculated from density measurements using a vibrating tube densitymeter. The performance of densitymeter was tested by measuring densities of benzene + cyclohexane mixtures (ref. 34). The densities agree with literature values within 1.0×10^{-5} g cm^{-3}.

RESULTS AND DISCUSSION

The excess molar enthalpies, excess molar heat capacities and excess molar volumes at $x = 0.5$ for a number of alkylbenzene mixtures containing benzene (or alkylbenzene) + alkylbenzene at 298.15 K and 308.15 K are summmarised in table 1. This also includes the results of other workers. The results in table 1 reveal that the sign of excess molar enthalpy is positive in all mixtures containing n-alkylbenzenes. However for mixtures containing isopropylbenzene excess molar enthalpy is positive with benzene but negative with toluene and ethylbenzene. The signs of excess molar heat capacities for all these mixtures are opposite of the excess molar enthalpies. The magnitudes of excess molar enthalpy, excess molar heat capacity and excess molar volume for all the mixtures containing n- alkylbenzenes depend on the difference ($n_2 - n_1$) of the chain lengths of the alkyl groups for the two components. The excess molar enthalpy increases with increase in ($n_2 - n_1$) while excess molar heat capacity decreases (i.e. it becomes more negative). Excess molar volumes show similar behaviour as excess molar enthalpies. The magnitudes of excess molar enthalpy and excess molar volume of systems containing benzene are much larger as compared to those found for mixtures containing toluene or other alkylbenzenes whose values for excess functions are comparable.
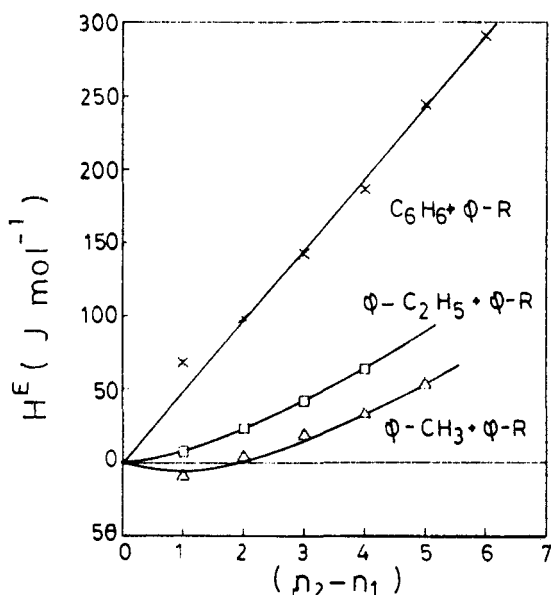

Fig 1. Excess molar enthalpies (x = 0.5 of benzene (or alkylbenzene) + alkyl benzene as a function of difference in chain lengths ($n_2 - n_1$) of alkyl groups of two components.
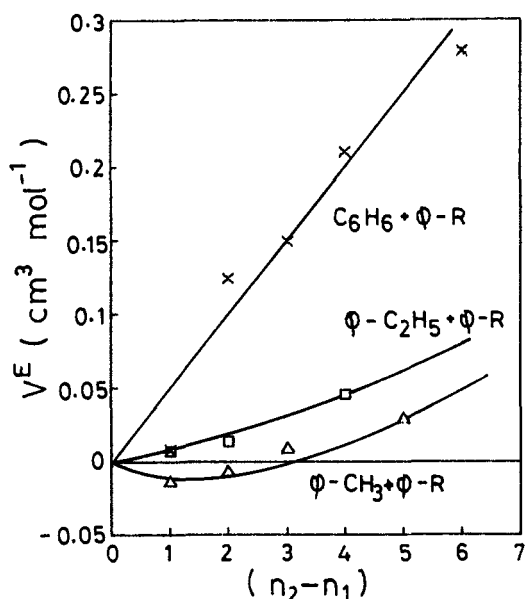
Fig 2. Excess molar volumes (x = 0.5) of benzene (or alkylbenzene) + alkylbenzene as a function of difference in chain lengths ($n_2 - n_1$) of alkyl groups of two components.

TABLE 1. Excess molar enthalpies, excess molar volumes and excess molar heat capacities and Flory's interaction parameter X_{12} for benzene (or alkylbenzene) + alkylbenzene mixtures at $x = 0.5$

System	T (K)	V^E (cm^3.mol^{-1})	H^E (J.mol^{-1})	C^E_p (J.K^{-1}.mol^{-1})	X_{12} (J.cm^{-3})
$C_6H_6 + C_6H_5CH_3$	298.15	0.008[a]	68.0[a]	-0.310[i]	4.3
$C_6H_6 + C_6H_5C_2H_5$	298.15	0.124[b]	98.0[f]	-0.815[i]	6.2
$C_6H_6 + C_6H_5n-C_3H_7$	298.15	0.149	142		9.90
	308.15	0.142	122	-2.2	9.01
$C_6H_6 + C_6H_5n-C_4H_9$	298.15	0.210	186	-1.38[j]	11.22
	308.15	0.197	172	-2.4[a]	10.63
$C_6H_6 + C_6H_5n-C_5H_{11}$	298.15		244[e]		
$C_6H_6 + C_6H_5n-C_6H_{13}$	298.15	0.277	291		16.30
	308.15	0.257	266	-2.5	15.14
$C_6H_6 + C_6H_5CH(CH_3)_2$	298.15	0.133	106		8.04
	308.15	0.129	98	-0.8	7.84
$C_6H_5CH_3 + C_6H_5C_2H_5$	298.15	-0.014[b]	-8.6[g]	0.052[i]	-0.34
$C_6H_5CH_3 + C_6H_5n-C_3H_7$	298.15	-0.007	4.6		0.959
	308.15	-0.007	4.2	-0.03	0.901
$C_6H_5CH_3 + C_6H_5n-C_4H_9$	298.15	0.009	19.1		1.263
	308.15	0.005	16.6	-0.21	1.092
$C_6H_5CH_3 + C_6H_5C_5H_{11}$	298.15		32.8[e]		
$C_6H_5CH_3 + C_6H_5n-C_6H_{13}$	298.15	0.029	53.0		2.836
	308.15	0.022	50.2	-0.36	2.612
$C_6H_5CH_3 + C_6H_5CH(CH_3)_2$	298.15	-0.029	-28.3		-0.494
	308.15	-0.028	-24.3	-0.28	-0.349
$C_6H_5C_2H_5 + C_6H_5n-C_3H_7$	298.15	0.007	8.0		0.531
	308.15	0.007	7.8	-0.02	0.511
$C_6H_5C_2H_5 + C_6H_5n-C_4H_9$	298.15	0.014	23.2		0.860
	308.15	0.014	21.3	-0.17	0.742
$C_6H_5C_2H_5 + C_6H_5C_5H_{11}$	298.15		41.8[e]		
$C_6H_5C_2H_5 + C_6H_5n-C_6H_{13}$	298.15	0.046	62.9	2.260	
	308.15	0.041	58.6	-0.48	2.017
$C_6H_5C_2H_5 +$	298.15		-3.69		0.034
$C_6H_5CH(CH_3)_2$	308.15		-2.86	0.06	0.071
$C_6H_5C_3H_7 + C_6H_5C_4H_9$	298.15		5.8[h]		
$C_6H_5C_3H_7 + C_6H_5C_5H_{11}$	298.15		16.5[e]		
$C_6H_5C_3H_7 + C_6H_5C_6H_{13}$	298.15		34.8[e]		
$C_6H_5C_4H_9 + C_6H_5C_5H_{11}$	298.15		5.3[e]		
$C_6H_5C_4H_9 + C_6H_5C_6H_{13}$	298.15		12.0[e]		
$C_6H_5C_5H_{11} + C_6H_5C_6H_{13}$	298.15		5.3[e]		

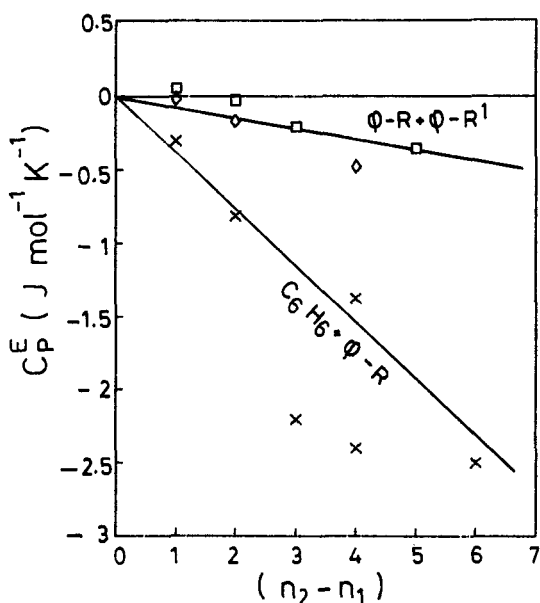[a] ref.25, [b] ref.39, [f] ref.26, [e] ref.29, [g] ref.37, [h] ref.28, [i] ref.27, [j] ref.38.

Fig 3. Excess molar heat capacities (x = 0.5) of benzene (or alkylbenzene) + alkylbenzene as a function of difference in chain lengths ($n_2 - n_1$) of alkyl groups of two components.
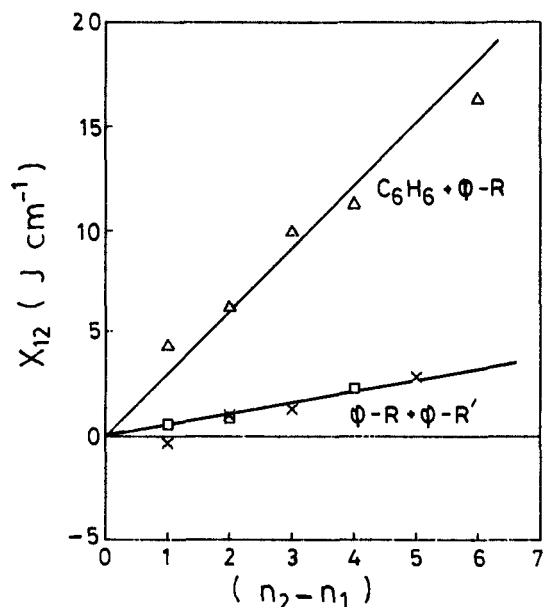
Fig 4. Flory's Interaction parameter X_{12} for benzene (or alkylbenzene) + alkyl benzene as a function of difference in chain lengths ($n_2 - n_1$) of alkyl groups of two components.

This difference in excess molar enthalpies and excess molar volumes between the mixtures of benzene and alkylbenzene and those containing alkylbenzenes cannot be explained in terms of dispersion interaction and free volume effect only. Depolarised Rayleigh scattering studies (ref. 8) and X-ray diffraction studies (ref. 9) indicate that on average, benzene molecules align themselves perpendicularly to each other. However, toluene and ethylbenzene show no such order correlations. The orientational order in benzene decreases with increase in temperature.

The orientational order in pure benzene would explain the large differences in excess molar enthalpy and excess molar volumes between mixtures containing benzene and toluene or higher alkylbenzenes. Similar arguments have been used in explaining excess molar enthalpies, excess molar volumes and excess molar gibb's energy of benzene + alkane mixtures (ref. 35)

It can be seen from table 1 that excess molar enthalpy for benzene + propylbenzene is larger than for benzene + isopropylbenzene and excess molar enthalpies for mixtures of toluene or ethylbenzene with propylbenzene are positive whereas mixtures of toluene or ethylbenzene with isopropylbenzene show negative excess moler enthalpies. The differences in excess molar enthalpies between two sets of results cannot be attributed to free volume effect because propylbenzene and isopropylbenzene have almost same free volumes. However, the difference in excess molar enthalpies is in line with the differences in their physical properties e.g. density, enthalpies of vapourisation. Negative excess molar enthalpies are sometimes attributed to specific interactions, however, it seems unlikely that such an interaction would exist between these hydrocarbons.

Table 1 also lists mean excess molar heat capacities for a number of binary mixtures in the temperature range 298.15 K - 318.15 K. The table also includes data from literature. It can be seen from the table that excess molar heat capacity is negative for all the mixtures except for toluene + ethylbenzene or isopropylbenzene and ethylbenzene + isopropylbenzene. Excess molar heat capacity for mixtures containing benzene show large negative values as compared to those found for mixtures containing toluene or ethylbenzene. However, excess molar heat capacity for mixtures containing toluene or ethylbenzene are small and comparable. The difference in magnitude of excess molar heat capacity between mixtures containing benzene and toluene or ethylbenzene can be explained by orientation order effects expected in mixtures containing benzene.

In Flory's theory (ref. 2,36) of mixtures of non-polar molecules two main contributions to excess thermodynamic properties are from free volume term and the dispersion type of interaction (considered to be independent of temperature). The latter is manifested by the interaction parameter X_{12} in Flory's theory. Figure 4 gives the plot of X_{12} so calculated by Flory's theory, using excess molar enthalpy data, as a function of ($n_2 - n_1$) where $n_2 > n_1$.

It can be seen that the entire data fall on two curves. The value of X_{12} for mixtures without benzene are small and as expected show some variation with respect to ($n_2 - n_1$). However, the values of X_{12} for mixtures containing benzene are much larger and fall on a separate curve. This implies that the values of X_{12} for mixtures containing benzene has contribution not only from dispersion interaction but from orientation order effects as well.

The chain length of the alkyl group is only up to six carbon atoms. It will be worthwhile to extend this work to higher alkylbenzenes.

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