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Excess Molar Volumes and Excess Molar Enthalpies of Quinoline + Aromatic Hydrocarbons at 303.15 K

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Excess molar volumes V_m^E and excess molar enthalpies H_m^E for quinoline + benzene, toluene, *o*-xylene, or *p*-xylene for the whole range of compositions have been measured at 303.15 K. The values of H_m^E and V_m^E for these mixtures suggest that quinoline is partly self-associated and there is strong interaction (weak hydrogen bonding) between quinoline and aromatic hydrocarbons. The values of V_m^E and H_m^E have also been computed from the Flory and Abe theory and Sanchez and Lacombe theory as well as from the Graph theory. All the theories correctly predict the sign or magnitude of H_m^E. Only the Graph theory is able to predict correctly the sign or magnitude of V_m^E; the other theories give a poor estimate of V_m^E.

Introduction

Our earlier studies (*1–3*) of excess molar volumes and excess molar enthalpies of 1,2-dibromoethane or ethyl iodide + an aromatic hydrocarbon have demonstrated the existence of weak specific interactions of the electron donor–acceptor type between the components in which the aromatic hydrocarbon behaves as the potential electron donor. The interaction of an aromatic hydrocarbon with N-bearing components appears to be equally interesting and needs to be investigated. With this viewpoint, the measurements of excess molar volumes and excess molar enthalpies for quinoline + benzene, toluene, *o*-xylene, or *p*-xylene at 303.15 K have been undertaken in order to understand the nature of molecular interactions of these binary mixtures. The applicability of the statistical mechanical theories of Flory and Abe (*4, 5*) and Sanchez and Lacombe (*6, 7*) as well as that of the Graph theoretical approach (*8, 9*) to our results has been critically examined.

Experimental Section

Quinoline, benzene, toluene, *o*-xylene, and *p*-xylene (Aldrich, AR grade) were purified by standard procedures (*10*). The purities of the final samples were checked by density determination at 303.15 ± 0.01 K which agreed to within ±5 × 10^{-5} g·cm^{-3} with the corresponding literature values (*11*) (quinoline, 1.085 79; benzene, 0.8685; toluene, 0.857 70; *o*-xylene, 0.871 60; *p*-xylene, 0.852 30 g·cm^{-3}). The excess molar volumes of quinoline + an aromatic hydrocarbon as a function of composition at 303.15 K were measured dilatometrically as described earlier (*12*). The temperature of the water bath was controlled to ±0.01 K. Excess molar enthalpies at 303.15 K were measured by a flow microcalorimeter (LKB-2107, LKB Broma, Sweden) as described by Monk and Wadso (*13*). Two identical Braun perfusor pumps and gas-tight Hamilton syringes were employed to pump liquids through the calorimeter. Using 10, 20, and 50 cm^3 syringes and 10-speed gear boxes on the perfusor pumps, different mixing ratios were achieved. The flow rates were determined by pumping distilled water through the calorimeter and weighing the amounts collected in a specific time interval. For each typical H_m^E measurement, different calibration constants were determined according to the flow rate, the amplification needed, and the composition of the mixture. The uncertainty in the measured H_m^E values is 1–2%.

Results and Discussion

The V_m^E and H_m^E for the binary mixtures of x C_9H_7N + (1 − x) C_6H_6, $C_6H_5CH_3$, *o*-$C_6H_4(CH_3)_2$, or *p*-$C_6H_4(CH_3)_2$ as a function of composition at 303.15 K are recorded in Tables I and II and shown graphically in Figures 1 and 2, respectively. The V_m^E for these mixtures are negative at all compositions while the H_m^E for the same set of mixtures are positive. The graphs of H_m^E vs x and V_m^E vs x are asymmetrical. The maximas are observed in the aromatic hydrocarbon rich region.

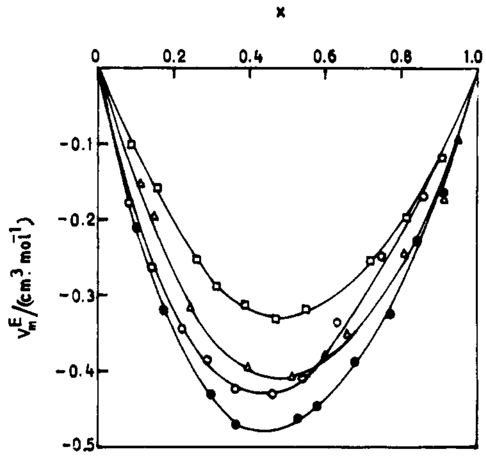

Figure 1. Excess molar volumes V_m^E at 303.15 for x C_9H_7N + ○, (1 − x) C_6H_6; ●, (1 − x) $C_6H_5CH_3$; □, (1 − x) *o*-$C_6H_4(CH_3)_2$; △, (1 − x) *p*-$C_6H_4(CH_3)_2$.

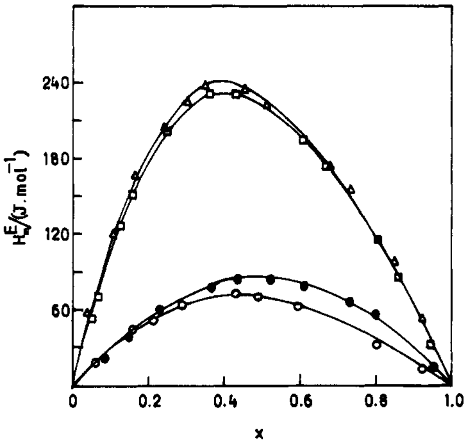

Figure 2. Excess molar enthalpies H_m^E at 303.15 K for x C_9H_7 N + ○, (1 − x) C_6H_6; ●, (1 − x) $C_6H_5CH_3$; □, (1 − x) *o*-$C_6H_4(CH_3)_2$; △, (1 − x) *p*-$C_6H_4(CH_3)_2$.

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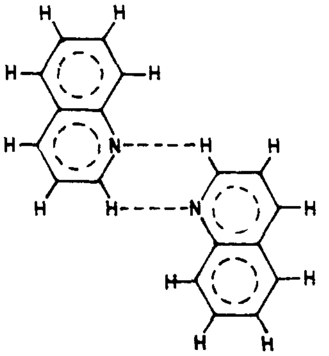

Figure 3. Self-association between quinoline molecules.

Table I. Experimental Excess Molar Volumes V_m^E for Quinoline + Aromatic Hydrocarbons at 303.15 K

x	V_m^E/ (cm^3·mol^{-1})	x	V_m^E/ (cm^3·mol^{-1})	x	V_m^E/ (cm^3·mol^{-1})
		x C_9H_7N + (1 - x) C_6H_6			
0.0812	−0.1751	0.3592	−0.4269	0.7458	−0.2495
0.1434	−0.2652	0.4611	−0.4290	0.8610	−0.1702
0.2185	−0.3454	0.5408	−0.4105		
0.2923	−0.3852	0.6290	−0.3384		
		x C_9H_7N + (1 - x) $C_6H_5CH_3$			
0.1063	0.2132	0.5252	−0.4669	0.8433	−0.2284
0.1766	−0.3206	0.5812	−0.4510	0.9110	−0.1701
0.2954	−0.4327	0.6748	−0.3900		
0.3596	−0.4728	0.7711	−0.3251		
		x C_9H_7N + (1 - x) o-$C_6H_4(CH_3)_2$			
0.0912	−0.1001	0.3921	−0.3151	0.8139	−0.1997
0.1581	−0.1576	0.4722	−0.3302	0.9120	−0.1201
0.2630	−0.2532	0.5496	−0.3183		
0.3136	−0.2903	0.7215	−0.2537		
		x C_9H_7N + (1 - x) p-$C_6H_4CH_3)_2$			
0.1102	−0.1526	0.5129	−0.4103	0.8050	−0.2519
0.1493	−0.1984	0.5537	−0.4078	0.9111	−0.1751
0.2397	−0.3180	0.6008	−0.3822	0.9478	−0.0940
0.3885	−0.3978	0.6569	−0.3545		

Table II. Experimental Excess Molar Enthalpies H_m^E for Quinoline + Aromatic Hydrocarbons at 303.15 K

x	H_m^E/ (J·mol^{-1})	x	H_m^E/ (J·mol^{-1})	x	H_m^E/ (J·mol^{-1})
		x C_9H_7N + (1 - x) C_6H_6			
0.0612	18.6	0.2913	63.1	0.6949	60.0
0.1553	42.1	0.4319	72.0	0.8013	30.9
0.2132	51.0	0.4925	68.2	0.9213	12.1
		x C_9H_7N + (1 - x) $C_6H_5CH_3$			
0.0812	21.5	0.4358	84.5	0.8013	57.1
0.1472	37.5	0.5213	84.4	0.9521	15.3
0.2272	60.0	0.6087	78.1		
0.3649	78.1	0.7341	66.1		
		x C_9H_7N + (1 - x) o-$C_6H_4(CH_5)_2$			
0.0512	54.2	0.2531	201.1	0.6732	173.3
0.0694	69.1	0.3621	229.5	0.8024	114.2
0.1272	126.2	0.5056	222.3	0.8521	84.2
0.1639	150.2	0.6121	195.1	0.9423	30.2
		x C_9H_7N + (1 - x) p-$C_6H_4(CH_3)_2$			
0.0412	56.1	0.3021	225.1	0.6781	174.2
0.1121	20.2	0.3449	237.2	0.7320	154.2
0.1669	65.1	0.4523	234.1	0.8473	97.0
0.2431	204.4	0.5112	219.9	0.9214	53.0

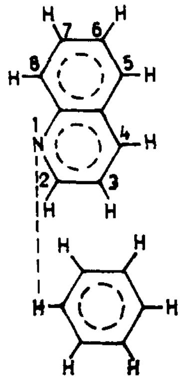

Figure 4. Intermolecular interactions shown in quinoline and aromatic hydrocarbon molecules.

Table III. Values of Parameters and Standard Deviations $s(M_m^E)$ for Quinoline + Aromatic Hydrocarbons at 303.15 K

C_9H_7N +	A_V	B_V	C_V	$s(V_m^E)$/(cm^3·mol^{-1})
C_6H_6	−1.6289	0.5772	−0.2874	0.0133
$C_6H_5CH_3$	−1.8767	0.2441	−0.3837	0.0133
o-$C_6H_4(CH_3)_2$	−1.3098	−0.1051	−0.0124	0.0123
p-$C_6H_4(CH_3)_2$	−1.6039	−0.1595	−0.2644	0.0211

C_9H_7N +	A_H	B_H	C_H	$s(H_m^E)$/(J·mol^{-1})
C_6H_6	270.9	−92.4	−47.4	1.2
$C_6H_5CH_3$	346.0	15.5	−31.2	2.7
o-$C_6H_4(CH_3)_2$	907.1	−317.0	−55.9	2.8
p-$C_6H_4(CH_3)_2$	902.7	−335.8	156.3	3.3

The experimental data of V_m^E and H_m^E have been fitted to the equation

$$M_m^E = x(1 - x)[A_M + B_M(2x - 1) + C_M(2x - 1)^2] \quad (1)$$

where x is the mole fraction of quinoline, M_m^E is V_m^E/(cm^3·mol^{-1}) or H_m^E/(J·mol^{-1}), and A_M, B_M, and C_M are fitted parameters. These parameters were evaluated by the method of least squares and are given together with the standard deviations (M_m^E) in Table III.

At the simplest qualitative level, the observed V_m^E and H_m^E values for quinoline and aromatic hydrocarbon mixtures may be accounted for if we assume that (i) quinoline is partly self-associated and there is a decrease in self-association when it is mixed with an aromatic hydrocarbon and (ii) there is strong interaction (most probably weak hydrogen bonding) between quinoline and aromatic hydrocarbon molecules. Morcom and Travers (*14*) have suggested that quinoline may be partly self-associated according to a hydrogen-bonding scheme similar to self-association in pyridine, and in view of this the self-association in quinoline may be represented as shown in Figure 3. Schaefer and Schneider (*15*) from the NMR studies of x C_9H_7N + (1 − x) C_6H_6 have reported maximum shielding of protons 3 and 4 and relatively less shielding of protons 2 and 8 of quinoline. It is most likely that benzene and quinoline are lying in parallel planes and the N atom of quinoline is lying directly above the H atom of benzene as shown in Figure 4. A similar parallel plane arrangement to explain the interactions between pyridine and benzene through hydrogen bonding has been suggested by Murrell and Gil (*16*). The interaction between quinoline and benzene is probably through weak hydrogen bonding. The positive values of H_m^E indicate that the effect due to factor i outweighs the effect due to factor ii. The introduction of one $-CH_3$ group in benzene (as in toluene) would increase the electron density, and hence toluene would have a higher electron donor capacity than benzene, and result in weaker bonding between the H atom associated with the C atom in the aromatic ring (which has less positive character) and the N atom of quinoline. This is supported by more positive H_m^E values for toluene than those for benzene. When two $-CH_3$ groups are introduced in benzene (as in xylenes), there is a further increase in the electron-donating capacity and the strength of the H···N interaction is weaker than that in toluene. This is again supported by more positive H_m^E values for xylenes than those for toluene.

A negative sign of V_m^E suggests strong interaction between quinoline and aromatic hydrocarbons. The magnitude of V_m^E

determines the extent of compactness, and this is more or less equal in the case of mixtures of x C_9H_7N + $(1 - x)$ C_6H_6 or p-$C_6H_4(CH_3)_2$. The mixtures of x C_9H_7N + $(1 - x)$ $C_6H_5CH_3$ provide a more compact arrangement; however, the arrangement of quinoline and o-xylene molecules is in a manner which causes an increase in volume and thus less negative V_m^E values.

Since the shape and size of the two kinds of molecules in these mixtures are different, it was thought worthwhile to examine our results in terms of the statistical theory of Flory and his colleagues (*4*, *5*) which takes into consideration the shape and size of the molecules. According to that theory, V_m^E and H_m^E for binary mixtures are given by

$$V_m{}^E = \tilde{V}^E_{\text{calcd}}\{xV_1{}^* + (1 - x)V_2{}^*\} \tag{2}$$

$$H_m{}^E = xP_1{}^*V_1{}^*(\tilde{V}_1{}^{-1} - \tilde{V}^{-1}_{\text{calcd}}) + (1 - x)P_2{}^*V_2{}^*(\tilde{V}_2{}^{-1} - \tilde{V}^{-1}_{\text{calcd}}) + xV_1{}^*\theta_2\chi_{12}\tilde{V}^{-1}_{\text{calcd}} \tag{3}$$

where all the symbols have the same significance as in the original papers (*4*, *5*). The coefficient of volume expansion (α) and isothermal compressibility (K_T) of pure components were taken from the literature (*17*, *18*). K_T of quinoline was evaluated from the following relation (*19*) as it was not available in the literature:

$$\delta^2 = \alpha T/K_T \tag{4}$$

where α is the coefficient of volume expansion and T is the temperature. The solubility parameter (δ) was evaluated using the following equation:

$$\delta = \left(\frac{\Delta H - RT}{V}\right)^{0.5} \tag{5}$$

where ΔH is the heat of vaporization, R is the gas constant, and V is the molar volume. There is reasonably good agreement between the experimental H_m^E values and those calculated using the theory of Flory for the mixtures of quinoline with aromatic hydrocarbons; for instance, at 0.3 mole fraction of quinoline the experimental H_m^E values and the calculated H_m^E values (given in parentheses) for quinoline + benzene (system A), quinoline + toluene (system B), quinoline + o-xylene (system C), and quinoline + p-xylene (system D) are 63.1 (59.6), 70.3 (74.3), 215.2 (191.7), and 223.0 (190.5) $J \cdot mol^{-1}$, respectively. However, the corresponding V_m^E values at this mole fraction are −0.4002 (0.1549), −0.4275 (0.0323), −0.2666 (0.1265), and −0.3323 (0.0884) $cm^3 \cdot mol^{-1}$ for systems A, B, C, and D, respectively, which show a poor agreement. It is evident from the results that the Flory theory is unable to predict even the sign of V_m^E values for these systems. The deviation is probably due to the errors in the coefficient of volume expansion (α) and isothermal compressibility (K_T) data of pure components which have been taken from the literature. The K_T value for quinoline is not reported in the literature, and hence an approximate value of K_T was evaluated from the heat of vaporization using eqs 4 and 5. Further, the deviation may also be due to the inability of the Flory theory to fully account for the packing effects.

V_m^E and H_m^E can be expressed in terms of the statistical theory of Sanchez and Lacombe (*6*, *7*) as

$$V_m{}^E = [1/\tilde{\rho}_{\text{mix}} - (\phi_1V_1 + \phi_2V_2)]r_{\text{mix}}V_{\text{mix}}{}^* \tag{6}$$

$$H_m{}^E = 2\phi_1\phi_2r_{\text{mix}}\tilde{\rho}_{\text{mix}}(\epsilon_{11}{}^* + \epsilon_{22}{}^* - 2\epsilon_{12}{}^*) + RTr_{\text{mix}}\left[\frac{\tilde{\rho}_1\phi_1{}^\circ - \tilde{\rho}_{\text{mix}}\phi_1}{\tilde{T}_1} + \frac{\tilde{\rho}_2\phi_2{}^\circ - \tilde{\rho}_{\text{mix}}\phi_2}{\tilde{T}_2}\right] \tag{7}$$

All the symbols have the same significance as described by Sanchez and Lacombe (*6*, *7*) in their original papers and the values of V_m^E and H_m^E were calculated as described by Sanchez and Lacombe. At 0.3 mole fraction of quinoline, the experimental H_m^E and those calculated using the Sanchez and Lacombe theory for systems A, B, C, and D, respectively, are 63.1 (90.5), 70.3 (81.9), 215.2 (199.8), and 223.0 (196.80) $J \cdot mol^{-1}$, and these results show that the Sanchez and Lacombe theory is able to predict the H_m^E values to a reasonably good degree. However, the corresponding V_m^E values at this mole fraction are −0.4002 (1.652), −0.4275 (1.008), −0.2666 (0.828), and −0.3323 (0.795) $cm^3 \cdot mol^{-1}$ for systems A, B, C, and D, respectively, and show a very poor agreement. The poor agreement between the calculated and experimental V_m^E values is due to the failure of the equation of state (used in the Sanchez and Lacombe theory) for these mixtures.

We also analyzed our results in terms of the Graph theoretical approach (*8*, *9*). According to this theory

$$V_m{}^E = \alpha_{12}[1/\sum x^3\xi_1 - \sum x/^3\xi_1] \tag{8}$$

and

$$H_m{}^E = x(1 - x)K_{12}\alpha_{12}'(^3\xi_1/^3\xi_2)/[x + (1 - x)K_{12}(^3\xi_1/^3\xi_2)] \tag{9}$$

where x, $1 - x$, $^3\xi_1$, and $^3\xi_2$ are the mole fractions and the corresponding third-degree connectivity parameters of molecules for components 1 and 2, respectively. The method of calculation of $^3\xi_1$ and $^3\xi_2$ is described elsewhere (*8*). In eq 8, α_{12} is a constant, characteristic of a particular mixture. Its value was calculated from the experimental value of V_m^E at 0.5 mole fraction, and then V_m^E at other mole fractions were evaluated using the same value of α_{12}. Equation 9 contains two unknown parameters, K_{12} and α_{12}', and these were evaluated by substituting experimental values at other mole fractions, i.e., 0.4 and 0.5. The H_m^E values at 0.3 mole fraction of quinoline for systems A, B, C, and D are 63.1 (64.3), 70.3 (70.91), 215.2 (218.0), and 223.0 (223.1) $J \cdot mol^{-1}$, respectively, and show a good agreement in sign as well in magnitude. The corresponding V_m^E values −0.4002 (−0.4114), −0.4275 (−0.4421), −0.2666 (−0.2830), and −0.3323 (−0.3580) $cm^3 \cdot mol^{-1}$ also give a reasonably good agreement.

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