

Excess molar enthalpies of several binary liquid mixtures containing either phenylmethylether (anisole) or benzaldehyde and an aromatic[☆]

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Abstract

For the 11 binary liquid systems [$x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)\{\text{C}_6\text{H}_6, \text{ or } \text{C}_6\text{H}_5\text{CH}_3, \text{ or } 1,2\text{-C}_6\text{H}_4(\text{CH}_3)_2, \text{ or } 1,3\text{-C}_6\text{H}_4(\text{CH}_3)_2, \text{ or } 1,4\text{-C}_6\text{H}_4(\text{CH}_3)_2, \text{ or } \text{C}_6\text{H}_5\text{C}_2\text{H}_5, \text{ or } 1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3, \text{ or } 1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3, \text{ or } \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2\}$] and [$x\text{C}_6\text{H}_5\text{CHO} + (1-x)\{\text{C}_6\text{H}_5\text{C}_2\text{H}_5, \text{ or } 1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3\}$], excess molar enthalpies H^E have been measured as a function of mole fraction x of either phenylmethylether (PME, anisole, methoxybenzene, $\text{C}_6\text{H}_5\text{OCH}_3$) or benzaldehyde (BA, $\text{C}_6\text{H}_5\text{CHO}$) at the temperature $T = 298.15$ K and atmospheric pressure. For these measurements, an LKB differential flow microcalorimeter equipped with two computer-controlled h.p.l.c. piston pumps (from Gilson) was used. For the mixtures of PME with an aromatic, the H^E -curves are all positive and rather small, and more or less parabolic; {PME + 1,3,5-trimethylbenzene (mesitylene)} exhibits the largest values: $H^E(x = 0.5) = 358 \text{ J mol}^{-1}$. The excess molar enthalpies of the mixtures of benzaldehyde with an aromatic are also all positive and rather small [e.g., for (BA + 1,3,5-trimethylbenzene) $H^E(x = 0.5) = 316 \text{ J mol}^{-1}$], though somewhat more skewed than those of the corresponding mixtures with PME.

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1. Introduction

Nonideal thermodynamic behavior of liquid mixtures may be heuristically discussed in terms of differences in: molecular size and shape, dispersion forces, polarity, polarizability, flexibility, molecular association, and so forth [1]. In many liquid mixtures, dipolar (and quadrupolar) interactions contribute significantly to the thermodynamic properties. When focussing on

molecules possessing a permanent electric dipole moment μ , one has to be aware, however, that this molecular quantity by itself is not particularly helpful in guiding the discussion. Advantageously, for the characterization of the *effective* polarity of a molecule, by virtue of the corresponding states principle one may define a reduced dipole moment $\tilde{\mu}$ [1,2] according to

$$(\tilde{\mu})^2 = \frac{\mu^2 N_A}{4\pi\epsilon_0 V_c k_B T_c} \quad (1)$$

Here ϵ_0 is the permittivity of vacuum, N_A the Avogadro's constant, k_B the Boltzmann's constant, V_c the critical molar volume, and T_c the critical temperature

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of the substance. However, even this quantity does not reflect adequately the increase of effective polarity which results from an unsymmetrical disposition of the polar groups within the molecule, i.e. from dipole moments exposed on the molecular periphery, in particular when interactions with molecules possessing high *local* polarizability, such as aromatics are considered (*aromatic effect* [3]).

In order to study the effects due to polar–polar and polar–nonpolar interactions, we have for quite some time investigated systematically some of the major excess quantities, i.e. excess molar enthalpy H^E , excess molar heat capacity C_p^E at constant pressure, and excess molar volume V^E of binary liquid mixtures containing at least one strongly polar component (see for instance, Refs. [4–12]). In this context we recently published a rather comprehensive paper on the thermodynamics of {benzonitrile (BN) + benzene, or toluene} [13]: the excess molar enthalpies of these two systems are highly unusual in that an *M-shaped* composition dependence is found, i.e. *two* maxima and *one* minimum are observed [14]. As far as we are aware, such a behavior of H^E has been found for two other systems only, namely (tetrachloromethane + toluene, or 1,3-dimethylbenzene) [15,16]. We analyzed these results assuming the formation of a 1:1 complex between BN and either benzene or toluene in conjunction with a simple lattice model for liquid mixtures due to McGlashan et al. [15]. Subsequently, the experimental basis was further enlarged by measuring H^E of BN mixed with several alkylsubstituted

benzenes, such as ethylbenzene, the three isomeric dimethylbenzenes (xylenes), isopropylbenzene, 1,2,4-trimethylbenzene (pseudocumene), and 1,3,5-trimethylbenzene (mesitylene) [17], where the electron donor strength increases roughly in this sequence. We note, however, that originally the focus was on (BN + toluene) for the following reasons: (i) both BN and toluene have about the same size and shape, and they are both aprotic “rigid” aromatic molecules; (ii) while toluene is essentially nonpolar, BN has a large permanent electric dipole moment ($\mu_{\text{BN}} = 13.94 \times 10^{-30}$ C m) [18]; (iii) whereas H^E of (BN + cyclohexane) at $T = 298.15$ K is positive and quite large and parabolic (at $x = 0.5$, $H^E = 1391$ J mol $^{-1}$ [14]), for (BN + toluene) H^E is much smaller and *M-shaped*: at $x = 0.5$, $H^E = -12$ J mol $^{-1}$. In continuation of this line of research, we present here excess molar enthalpies of nine mixtures {phenylmethylether (PME, anisole, methoxybenzene, C₆H₅OCH₃) + an aromatic}, and of {benzaldehyde (BA, C₆H₅CHO) + ethylbenzene, or 1,3,5-trimethylbenzene} at $T = 298.15$ K and ambient pressure. Both PME and BA have molecular shapes comparable with that of BN, yet, they are not as “rigid”, and they are distinctly less polar: the permanent electric dipole moment of PME is about one-third that of BN, while that of BA is about two-thirds. The methoxy group as well as the aldehyde group are capable of rotation along, respectively, the C–O bond and the C–C bond connecting them to the aromatic ring. The aromatics are essentially nonpolar. Table 1 summarizes the

Table 1

Densities ρ^* of the pure liquids at $T = 298.15$ K and atmospheric pressure (measured with a vibrating-tube densimeter) and dipole moments μ

Substance	$\rho^*/(\text{g cm}^{-3})$		$10^{30} \times \mu/(\text{C m})^b$
	This work	Literature ^a	
Benzene	0.87363	0.87367	0
Toluene	0.86218	0.86223	1.20
1,2-Dimethylbenzene (<i>o</i> -xylene)	0.87555	0.87601	1.80
1,3-Dimethylbenzene (<i>m</i> -xylene)	0.85968	0.85991	1.03
1,4-Dimethylbenzene (<i>p</i> -xylene)	0.85647	0.85667	0
Ethylbenzene	0.86241	0.86196	1.23
1,2,4-Trimethylbenzene (pseudocumene)	0.87199	0.87244	1.00
1,3,5-Trimethylbenzene (mesitylene)	0.86151	0.86112	0
Isopropylbenzene (cumene)	0.85758	0.85763	1.33
Phenylmethylether (anisole)	0.99022	0.98931	4.17
Benzaldehyde	1.04138	1.04320	9.94

^a Ref. [23].

^b Refs. [18–20].

dipole moments of all substances used in this work [18–20]. For the critical quantities T_c and V_c , see Reid et al. [21].

2. Experimental

Chemicals. Benzene and toluene were puriss. p.a. quality from Fluka, with purities exceeding 99.5 mol%. Ethylbenzene, 1,2-dimethylbenzene (*o*-xylene), 1,3-dimethylbenzene (*m*-xylene), 1,4-dimethylbenzene (*p*-xylene), 1,2,4-trimethylbenzene (pseudocumene), 1,3,5-trimethylbenzene (mesitylene), and benzaldehyde were puriss. p.a. quality from Fluka, with purities exceeding 99 mol%, and isopropylbenzene (cumene) and phenylmethylether (anisole, methoxybenzene) were from Aldrich with purities exceeding 99 mol%. All liquids were carefully dried with molecular sieve and used without further purification. Table 1 also contains the densities ρ^* at $T = 298.15$ K and ambient pressure of the pure liquids as measured with a vibrating-tube densimeter (model 02D, from Sodev). In general, agreement with reliable literature data is satisfactory [22,23].

Calorimetry. Excess molar enthalpies were determined at $T = 298.15$ K and atmospheric pressure using a differential flow microcalorimeter from LKB (model 2107-121) operating under constant flow conditions [24], incorporating, however, some modifications of equipment as described previously [13,25]. In particular, the flow rates of the two liquids to be mixed are kept constant by using two computer-controlled h.p.l.c. piston pumps from Gilson (models 305 and 306). Prior to the actual experiments, the flow rates were calibrated by mass, covering essentially the whole composition range. Since the residence time in the mixing chamber guaranteeing complete mixing may vary considerably with the type of mixture, the optimum flow rates have to be determined experimentally. We did not observe any dependence of the results on the total flow rate, provided it was kept smaller than about $10 \mu\text{l s}^{-1}$. The performance of the calorimeter was routinely checked by measuring H^E at $T = 298.15$ K of selected test mixtures over the entire composition range, such as benzene + cyclohexane. Agreement with recommended literature data [26] was always satisfactory, that is to say, differences were below 0.5% over most of the composition range.

3. Results and discussion

Table 2 summarizes the experimental results for the excess molar enthalpies of the 11 systems studied, while graphical representations are provided by Figs. 1–3. For each mixture, the experimental data were fitted with a Redlich–Kister type smoothing function

$$H^E / (\text{J mol}^{-1}) = x(1-x) \sum_{i=0}^k A_i (2x-1)^i. \quad (2)$$

The values of the $k+1$ coefficients A_i and the corresponding standard deviations s are given in Table 3.

Excess molar enthalpies of mixtures belonging to the set of systems investigated, i.e. (PME + an aromatic) and (BA + an aromatic), are surprisingly scarce [27,28]. The data reported by Viswanathan et al. [29] on (PME + benzene) are distinctly larger

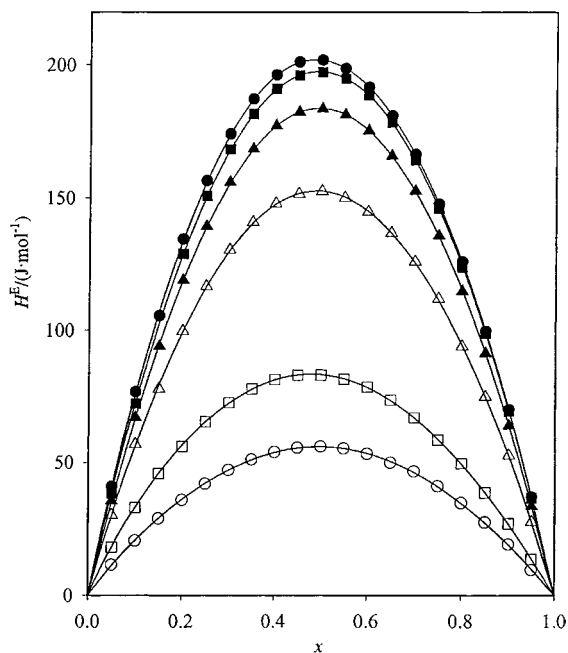


Fig. 1. Excess molar enthalpies H^E of {Phenylmethylether (anisole) + an aromatic} as a function of mole fraction x at $T = 298.15$ K and atmospheric pressure. Experimental results: (○) $\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)\text{C}_6\text{H}_6\}$; (□) $\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)\text{C}_6\text{H}_5\text{CH}_3\}$; (△) $\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)\text{C}_6\text{H}_5\text{C}_2\text{H}_5\}$; (▲) $\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,4\text{-C}_6\text{H}_4(\text{CH}_3)_2\}$; (■) $\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,3\text{-C}_6\text{H}_4(\text{CH}_3)_2\}$; (●) $\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,2\text{-C}_6\text{H}_4(\text{CH}_3)_2\}$. The solid curves were calculated by using Eq. (2) with parameters from Table 3.

Table 2

Excess molar enthalpies H^E at the temperature $T = 298.15$ K and atmospheric pressure of {Phenylmethylether (anisole) + an aromatic} and {banzaldehyde + an aromatic}

x	H^E (J mol ⁻¹)										
	{ x C ₆ H ₅ OCH ₃ +(1- x) C ₆ H ₆ }	{ x C ₆ H ₅ OCH ₃ +(1- x) C ₆ H ₅ CH ₃ }	{ x C ₆ H ₅ OCH ₃ +(1- x)1,2-C ₆ H ₄ (CH ₃) ₂ }	{ x C ₆ H ₅ OCH ₃ +(1- x)1,3-C ₆ H ₄ (CH ₃) ₂ }	{ x C ₆ H ₅ OCH ₃ +(1- x)1,4-C ₆ H ₄ (CH ₃) ₂ }	{ x C ₆ H ₅ OCH ₃ +(1- x) C ₆ H ₅ C ₂ H ₅ }	{ x C ₆ H ₅ OCH ₃ +(1- x) 1,2,4-C ₆ H ₃ (CH ₃) ₃ }	{ x C ₆ H ₅ OCH ₃ +(1- x) 1,3,5-C ₆ H ₃ (CH ₃) ₃ }	{ x C ₆ H ₅ OCH ₃ +(1- x) C ₆ H ₅ CH (CH ₃) ₂ }	{ x C ₆ H ₅ CHO +(1- x) C ₆ H ₅ C ₂ H ₅ }	{ x C ₆ H ₅ CHO +(1- x) 1,3,5-C ₆ H ₃ (CH ₃) ₃ }
0.0500	11.49	18.08	40.84	38.37	35.59	30.19	63.33	66.19	40.21	52.83	79.65
0.1000	20.57	33.02	76.76	72.30	67.01	56.86	121.98	126.26	75.08	95.81	142.39
0.1500	28.84	45.80	105.42		93.97	77.83	172.46	178.96	106.70	130.19	194.95
0.2000	35.89	56.03	134.32	128.72	118.72	99.58	216.02	225.79	133.28	154.69	235.92
0.2500	41.91	65.40	156.53	150.77	139.24	116.42	253.09	265.80	155.64	173.55	267.06
0.3000	47.10	72.60	174.01	168.23	155.88	130.26	282.98	297.93	173.65	185.56	293.83
0.3500	51.07	77.85	187.14	181.48	168.42	140.75	305.87	323.51	187.21	192.33	308.19
0.4000	53.90	81.41	196.20	190.94	177.12	147.89	322.15	342.07	196.58	204.22	316.15
0.4500	55.56	83.04	201.07	196.00	182.16	151.57	331.75	352.71	201.32	204.71	314.77
0.5000	56.00	83.05	201.80	197.35	183.45	152.50	334.65	357.25	202.30	201.83	316.00
0.5500	55.27	81.53	198.62	194.81	181.19	150.03	330.96	354.72	199.41	195.23	308.39
0.6000	53.28	78.53	191.50	188.59	175.25	144.74	321.14	345.31	192.65	185.69	295.15
0.6500	49.91	73.69	180.77	178.38	165.82	136.68	304.49	328.40	181.86	170.72	277.96
0.7000	46.62	66.97	166.34	164.28	152.65	125.77	281.74	304.88	167.54	156.09	254.56
0.7500	41.03	58.56	147.73	145.97	135.68	111.77	252.17	273.47	149.18	137.36	225.92
0.8000	34.72	49.65	125.76	123.60	114.56	93.89	215.71	234.45	126.59	115.63	191.73
0.8500	27.48	38.59	99.60	98.80	91.25	74.79	172.05	188.45	100.34	90.75	151.15
0.9000	19.16	27.00	70.00	69.34	63.90	52.62	122.36	133.40	70.11	63.89	105.65
0.9500	9.55	13.65	36.92	36.61	33.67	27.70	64.47	71.13	37.10	33.69	54.59

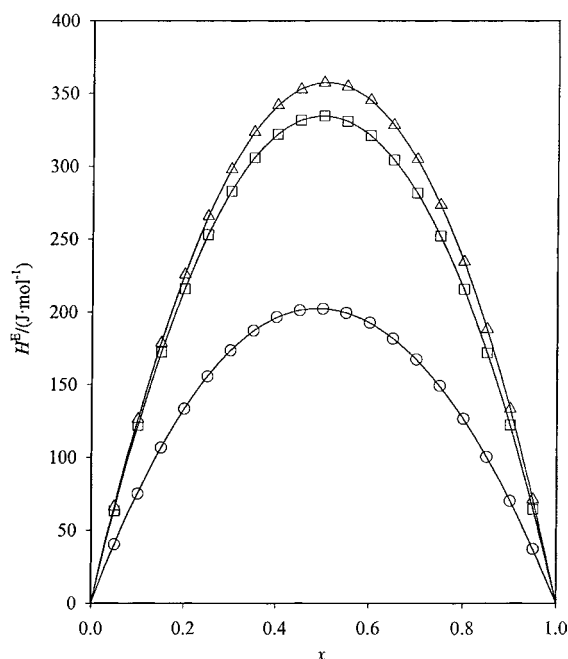


Fig. 2. Excess molar enthalpies H^E of {Phenylmethylether (anisole) + an aromatic} as a function of mole fraction x at $T = 298.15$ K and atmospheric pressure. Experimental results: (○) $\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2\}$; (□) $\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,2,4\text{-C}_6\text{H}_3\text{-(CH}_3)_3\}$; (△) $\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3\}$. The solid curves were calculated by using Eq. (2) with parameters from Table 3.

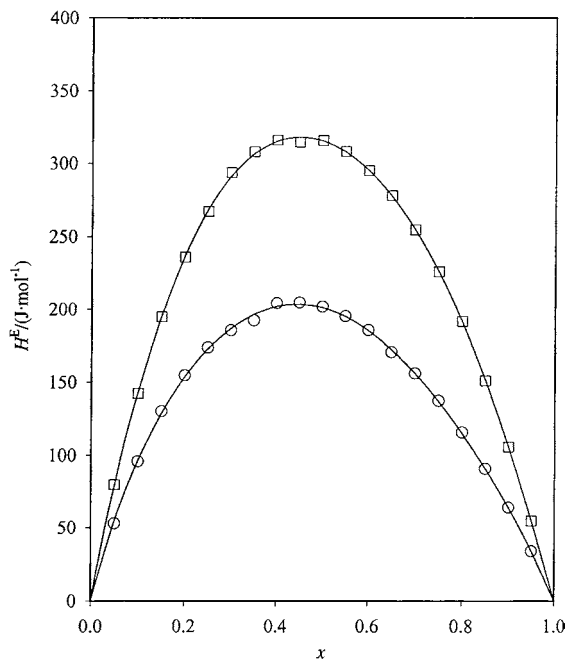


Fig. 3. Excess molar enthalpies H^E of {benzaldehyde + an aromatic} as a function of mole fraction x at $T = 298.15$ K and atmospheric pressure. Experimental results: (○) $\{x\text{C}_6\text{H}_5\text{CHO} + (1-x)\text{C}_6\text{H}_5\text{C}_2\text{H}_5\}$; (□) $\{x\text{C}_6\text{H}_5\text{CHO} + (1-x)1,3,5\text{-C}_6\text{H}_3\text{-(CH}_3)_3\}$. The solid curves were calculated by using Eq. (2) with parameters from Table 3.

than ours (by ca. 30%) and show considerable scatter. Considering the smallness of the excess molar enthalpy of (PME + ethylbenzene), the values measured by Kehiaian et al. [30], though 5% lower around

equimolar composition, are still in reasonable agreement with our results. The partial molar enthalpy at infinite dilution of PME in 1,3,5-trimethylbenzene has been determined by Fuchs et al. [31], though with

Table 3

Parameters A_i and standard deviations s for least-squares representation by Eq. (1) of $H^E/(\text{J mol}^{-1})$ for {Phenylmethylether (anisole) + an aromatic} and {benzaldehyde + an aromatic} at the temperature $T = 298.15$ K and atmospheric pressure

	$A_0/(\text{J mol}^{-1})$	$A_1/(\text{J mol}^{-1})$	$A_2/(\text{J mol}^{-1})$	$A_3/(\text{J mol}^{-1})$	$A_4/(\text{J mol}^{-1})$	$s/(\text{J mol}^{-1})$
$\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)\text{C}_6\text{H}_6\}$	223.85	-2.68	-12.71	-12.71	12.38	0.26
$\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)\text{C}_6\text{H}_5\text{CH}_3\}$	333.10	-28.97	-11.30	-21.88	15.37	0.23
$\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,2\text{-C}_6\text{H}_4(\text{CH}_3)_2\}$	807.54	-47.32	12.84	10.15	-9.01	0.59
$\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,3\text{-C}_6\text{H}_4(\text{CH}_3)_2\}$	790.01	-25.48	7.57	5.03	-16.69	0.24
$\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,4\text{-C}_6\text{H}_4(\text{CH}_3)_2\}$	734.63	-18.95	-7.89	-1.26	-7.82	0.31
$\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)\text{C}_6\text{H}_5\text{C}_2\text{H}_5\}$	610.44	-28.46	-16.74	6.31	10.36	0.55
$\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,2,4\text{-C}_6\text{H}_3(\text{CH}_3)_3\}$	1338.35	-11.77	42.94	24.56	-31.61	0.26
$\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3\}$	1429.58	35.03	37.39	28.65	-26.81	0.27
$\{x\text{C}_6\text{H}_5\text{OCH}_3 + (1-x)\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2\}$	809.77	-37.60	17.50	5.04	-26.87	0.23
$\{x\text{C}_6\text{H}_5\text{CHO} + (1-x)\text{C}_6\text{H}_5\text{C}_2\text{H}_5\}$	804.8	-168.2	54.2	-89.3	122.9	1.6
$\{x\text{C}_6\text{H}_5\text{CHO} + (1-x)1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3\}$	1262.3	-206.8	252.2	-80.7	-107.9	1.4

quite a large uncertainty (at least $\pm 200 \text{ J mol}^{-1}$). Their value, $H_{\text{PME}}^{\text{E}\infty}$ (FPS) = 1.59 kJ mol^{-1} , compares satisfactorily with the 1.38 kJ mol^{-1} obtained through extrapolation from our measurements according to

$$H_{\text{PME}}^{\text{E}\infty} = \sum_{i=0}^k A_i (-1)^i \quad (3)$$

No other results could be found for comparison. We note, however, the recent measurements of H^{E} of the technically important mixtures (BA + benzene, or toluene) at elevated temperatures (323.15–413.15 K), issuing from Gmehling's laboratory in Oldenburg [32]. When extrapolated to 298.15 K, their data for (BA + benzene) agree reasonably well with those of Ferino et al. [33].

Qualitatively, the experimental results may be rationalized in terms of the KGB group contribution theory [34,35] in the random mixing approximation (though it cannot differentiate between positional isomers, such as between 1,2-dimethylbenzene and 1,3-dimethylbenzene). For instance, when going from {PME + C_6H_6 } to {PME + $\text{C}_6\text{H}_3(\text{CH}_3)_3$ }, the increasing alkyl substitution—and thus the increasing molecular aliphatic surface fraction of the aromatic component—leads to more positive excess enthalpies. However, excess enthalpies of {BA + $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$, or 1,3,5- $\text{C}_6\text{H}_3(\text{CH}_3)_3$ } are smaller than those of the analogous mixtures with PME, despite $\mu_{\text{BA}} \approx 2\mu_{\text{PME}}$, which fact is not readily understood unless specific interactions (weak associations) are invoked. In terms of Pople's [36] approach, the contribution to H^{E} resulting from a net destruction of order due to mixing the polar liquid with a nonpolar liquid is positive and proportional to $\mu_1^4/(VT)^2$, where V denotes the molar volume, see Wilhelm [12]. Indeed, results for the analogous mixtures with cyclohexane qualitatively confirm this prediction: H^{E} of (BA + cyclohexane) is more positive than H^{E} of (PME + cyclohexane) [37]. Evidently, more experimental information is needed to clarify this issue.

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