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THERMODYNAMICS OF MOLECULAR INTERACTIONS IN BINARY MIXTURES OF NON-ELECTROLYTES. MOLAR EXCESS VOLUMES

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ABSTRACT

Molar excess volumes, V^E, for pyridine (A) + α-picoline (B), + β-picoline (B) and + γ-picoline (B) and benzene (A) + toluene (B), + *o*-xylene (B) and + *p*-xylene (B) and carbon tetrachloride (A) + *n*-heptane (B) have been measured dilatometrically as a function of temperature and composition and have been utilized to study B–B and B–B–B interactions in the presence of A via the Mayer–McMillan approach. A model has also been presented to account for these B–B and B–B–B interactions. The V^E data at 308.15 K have also been analysed in terms of the "graph theoretical" approach which describes the V^E data well for all these mixtures at 308.15 K. The "graph theoretical" approach has further been extended to successfully evaluate V^E data for a mixture at any temperature, T_2, when the V^E data at T_1 are known.

INTRODUCTION

Since thermodynamic excess functions are a measure of solute (B)–solvent (A) interactions and as an (A + B) binary solution of non-electrolyte may be assumed to have been formed by the replacement of like contacts in the pure A and B by unlike (A–B) contacts in the mixture, it appears that thermodynamic excess functions for binary mixtures of non-electrolytes could be utilized to see how the like interactions in the pure (say) B are influenced by the presence of the pure A in the (A + B) mixture. Again, as the mathematical discipline of graph theory [1,2] has been utilized to determine [2,3] the relationship between the structure of a molecule and its physical and chemical properties, it was felt that it should also be able to explain thermodynamic excess functions of binary mixtures. These arguments formed the basis of an approach, henceforth called the "graph-theoretical approach", that employed the graph-theoretical connectivity parameters of the third degree, ${}^3\xi$, of the molecules concerned to successfully describe [4,5] not only

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the molar excess volumes, V^E, and molar excess enthalpies, H^E, of binary mixtures of non-electrolytes (other than heterocyclics), but also the V^E of ternary mixtures of non-electrolytes [6] (other than heterocyclics). The present work deals with the measurement of V^E of pyridine (A) + α-picoline (B), + β-picoline (B) and + γ-picoline (B), benzene (A) + toluene (B), + *o*-xylene (B) and + *p*-xylene (B) and carbon tetrachloride (A) + *n*-heptane (B) in order to study the influence of A on the (B–B) interactions in these (A + B) binary mixtures and also to see as to how the "graph-theoretical" approach could be utilized to explain these V^E data as a function of temperature.

EXPERIMENTAL

Benzene, toluene, *o*-xylene, *p*-xylene, pyridine, α-picoline, β-picoline, γ-picoline, *n*-heptane and carbon tetrachloride (all B.D.H. Analar grade) were purified by standard procedures [7]. The purities of the final samples were checked by determining their densities at 298.15 ± 0.01 K and these agreed to within 0.00005 g cm^{-3} with the corresponding literature values [8–12].

Molar excess volumes were measured dilatometrically in the manner described earlier [13]. The temperature of the bath was controlled to ±0.01 K and the uncertainty in our measured V^E values was about 0.4%.

RESULTS

V^E data for the various mixtures are recorded in Table 1 and were expressed as

$$\frac{V^E}{x_1x_2} = \sum_{n=0}^{2} V_n(x_1 - x_2)^n \qquad (1)$$

where V_n ($n = 0$–2) are adjustable parameters and x_1 is the mole fraction of component 1. The V_n parameters were obtained by fitting the experimental V^E/x_1x_2 data to eqn. (1) by the method of least squares and are recorded together with the standard deviations, $\sigma(V^E)$, of V^E in Table 2.

DISCUSSION

Our V^E data at 298.15 K for benzene + toluene, + *o*-xylene and + *p*-xylene compare well, within the experimental uncertainties, with the corresponding best available literature values [13–15]. We are, however, unaware of any V^E data with which to compare our V^E data for the rest of the mixtures.

The V^E data were next utilized to study the influence of A on the (B–B)

TABLE 1

Measured V^E values for various mixtures

x_1	V^E (cm^3 mole^{-1})	x_1	V^E (cm^3 mole^{-1})
Pyridine(i) + α-picoline(j)			
308.15 K			
0.1701	0.012	0.4862	0.032
0.2238	0.019	0.5160	0.034
0.2554	0.023	0.6312	0.033
0.4225	0.030	0.7582	0.024
0.4855	0.036		
318.15 K			
0.1604	0.073	0.7517	0.102
0.3152	0.106	0.8585	0.070
0.3292	0.106	0.9201	0.009
0.3318	0.110	0.9400	0.006
0.4860	0.127	0.9502	0.005
0.7121	0.110	0.9589	0.004
Pyridine(i) + β-picoline(j)			
308.15 K			
0.0524	0.007	0.5324	0.028
0.1356	0.017	0.5983	0.028
0.1463	0.017	0.7365	0.023
0.2481	0.023	0.7472	0.023
0.3792	0.027	0.9036	0.012
0.5045	0.027		
318.15 K			
0.1604	0.030	0.6863	0.048
0.2231	0.038	0.7891	0.031
0.3114	0.048	0.9101	0.010
0.5120	0.060	0.9310	0.009
0.5244	0.061	0.9390	0.008
0.6338	0.050	0.9505	0.006
Pyridine(i) + γ-picoline(j)			
308.15 K			
0.1573	0.020	0.5627	0.037
0.2643	0.030	0.6444	0.032
0.4231	0.039	0.7720	0.025
0.4981	0.037	0.9327	0.011
0.5482	0.037		
318.15 K			
0.2274	0.032	0.7843	0.025
0.3112	0.041	0.9201	0.010
0.3677	0.044	0.9315	0.008
0.4102	0.046	0.9450	0.007
0.6024	0.041	0.9501	0.006
0.6448	0.037		

TABLE 1 (continued)

x_1	V^E (cm^3 $mole^{-1}$)	x_1	V^E (cm^3 $mole^{-1}$)
Benzene(i) + toluene(j)			
298.15 K			
0.0833	0.019	0.5183	0.084
0.1542	0.035	0.6376	0.075
0.2187	0.050	0.7511	0.056
0.3374	0.072	0.8602	0.032
0.3965	0.079	0.9402	0.013
308.15 K			
0.0401	0.007	0.8614	0.036
0.0157	0.021	0.9122	0.024
0.2228	0.049	0.9250	0.022
0.3082	0.067	0.9338	0.018
0.4343	0.087	0.9414	0.016
0.4912	0.089		
0.5706	0.084		
0.6902	0.075		
0.7762	0.058		
Benzene(i) + o-xylene(j)			
298.15 K			
0.0855	0.071	0.5561	0.257
0.2248	0.171	0.6152	0.251
0.2680	0.198	0.7773	0.179
0.3505	0.229	0.8586	0.122
0.4211	0.255	0.9679	0.031
0.4998	0.260		
308.15 K			
0.0792	0.041	0.7166	0.209
0.1411	0.079	0.8017	0.159
0.2308	0.138	0.9104	0.080
0.3478	0.205	0.9198	0.069
0.4314	0.239	0.9281	0.060
0.5049	0.251	0.9494	0.041
0.5768	0.251		
Benzene(i) + p-xylene(j)			
298.15 K			
0.1228	0.067	0.5299	0.209
0.2426	0.130	0.6229	0.206
0.3299	0.165	0.7616	0.160
0.4528	0.203	0.9248	0.059
0.4910	0.209		
308.15 K			
0.0412	0.021	0.7154	0.174
0.1211	0.063	0.8929	0.081
0.2148	0.114	0.9186	0.052

TABLE 1 (continued)

x_1	V^E (cm^3 mole^{-1})	x_1	V^E (cm^3 mole^{-1})
0.3561	0.165	0.9205	0.050
0.4407	0.195	0.9476	0.026
0.4970	0.204	0.9526	0.025
0.5855	0.205		
Carbon tetrachloride(i) + n-heptane(j)			
298.15 K			
0.1199	0.045	0.5641	0.127
0.2406	0.084	0.6205	0.116
0.3721	0.112	0.7253	0.104
0.3778	0.114	0.8781	0.063
308.15 K			
0.1285	0.060	0.5000	0.134
0.2278	0.089	0.5154	0.137
0.3598	0.123	0.6521	0.128
0.3654	0.118	0.7576	0.111
0.4266	0.130	0.8563	0.079

TABLE 2

Parameters V_n ($n = 0$–2) of eqn. (1) and the standard deviations, $\sigma(V^E)$, of V^E for the various mixtures

Mixture	Temp. (K)	V_0	V_1	V_2	$\sigma(V^E)$ (cm^3 mole^{-1})
Pyridine(*i*)+ α-picoline(*j*)	308.15	0.140	0.018	−0.056	0.002
	318.15	0.504	0.035	0.094	0.002
Pyridine(*i*)+ β-picoline(*j*)	308.15	0.108	−0.004	0.050	0.002
	318.15	0.236	−0.019	−0.094	0.002
Pyridine(*i*)+ γ-picoline(*j*)	308.15	0.150	−0.024	−0.190	0.002
	318.15	0.180	−0.044	−0.044	0.001
Benzene(*i*)+ toluene(*j*)	298.15	0.336	0.0001	−0.131	0.001
	308.15	0.360	0.044	−0.1719	0.001
Benzene(*i*)+ *o*-xylene(*j*)	298.15	1.060	0.050	−0.187	0.001
	308.15	1.005	0.215	−0.382	0.001
Benzene(*i*)+ *p*-xylene(*j*)	298.15	0.840	0.163	−0.188	0.001
	308.15	0.820	0.163	−0.188	0.001
Carbon tetrachloride(*i*)+ *n*-heptane(*j*)	298.15	0.500	0.045	−0.038	0.001
	308.15	0.540	0.074	0.088	0.002

interactions in these binary mixtures.

Although several thermodynamic techniques [16] can be employed for the purpose, the Mayer–McMillan formalism [17] appears to be an attractive one. According to this treatment, any changes in the properties of the solvent appear in the magnitudes of the solute–solute virial coefficients and the self-interaction coefficients for a binary system remain unchanged when an additional solute is added to this binary system. This is expected to be true for these binary mixtures since the solute–solute interactions would be of a short-range nature. According to this formalism [17], V_1^E of a solution containing n solute species can be expressed as

$$V_1^E(m_i \ldots m_n) = V - V_{\text{sol}} - \sum_{i=1}^{n} V_1^0 n_i \tag{2}$$

$$= \sum_{i=1}^{n} \sum_{j=1}^{n} V_{ij} m_i m_j + \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} V_{ijk} m_i m_j m_k + \ldots \tag{3}$$

where V and $V_1^E(m_i \ldots m_n)$ are the volumes and excess volumes, respectively, of a solution containing 1 kg of solvent (A) and $m_i \ldots m_n$ moles of each solute species, V_{sol} is the standard volume of 1 kg of A and V_i^0 is the partial molar volume of each solute. For a binary (A + B) solution, eqn. (3) reduces to

$$V_{(i)}^E(m_B) = V_{BB} m_B^2 + V_{BBB} m_B^3 + \ldots \tag{4}$$

Evaluation of V_{BB} and V_{BBB} parameters of eqn. (4) envisages that V^E and x_B data for the various (A + B) mixtures should be converted to $V_1^E(m_B)$ and m_B and this was achieved by means of the relations [6]

$$V_1^E(m_B) = \frac{V^E(x_B)\ (\text{cm}^3\ \text{mole}^{-1})}{x_A} \left[\frac{1000}{\text{Mol. wt. of A}} \right] \tag{5}$$

and

$$m_B = \frac{x_B \times 1000}{x_1 \times \text{M.W. of A}} \tag{6}$$

In order that the contributions of multiple solute–solute interactions to the observed V^E data are minimum, it is necessary that V^E data for dilute solutions should be utilized to evaluate V_{BB} and V_{BBB} from eqn. (4) by means of eqns. (5) and (6). Consequently, we employed our $V^E(x_B)$ data in the range $0.1 \leqslant x_B \leqslant 0.05$ corresponding to $1.3 \leqslant m_B \leqslant 0.05$ to evaluate $V_1^E(m_B)$ and m_B and hence V_{BB} and V_{BBB} from the intercept and slope of the plot of $V_1^E(m_B)/m_B^2$ vs. m_B, which are almost linear in this composition range. Such V_{BB} and V_{BBB} values for the various solutes in the presence of A are recorded in Table 3.

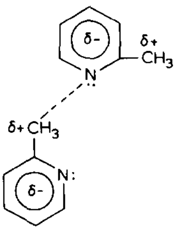
Examination of Table 3 shows that, while the V_{BB} for the various picolines in the presence of pyridine vary in the sequence α-picoline < β-picoline < γ-

TABLE 3

Self (solute–solute) volume interaction coefficients at 308.15 K

Mixture	V_{BB}	V_{BBB}
Pyridine(i)+ α-picoline(j)	0.25	−0.139
Pyridine(i)+ β-picoline(j)	0.28	−0.159
Pyridine(i)+ γ-picoline(j)	0.29	−0.143
Benzene(i)+ toluene(j)	0.51	−0.263
Benzene(i)+ o-xylene(j)	2.38	−1.563
Benzene(i)+ p-xylene(j)	1.20	−0.625
Carbon tetrachloride (i)+ n-heptane(j)	1.55	−1.191

picoline, those of toluene, o-xylene and p-xylene in the presence of benzene vary as toluene < p-xylene < o-xylene. This is understandable. The presence of a $-CH_3$ substituent at the position α to the N atom in α-picoline renders the lone electron pair on the N atom more labile so that when another α-picoline molecule approaches the first, the electron-deficient $-CH_3$ end of the approaching molecule may interact as



Since the influence of the $-CH_3$ substituent in picoline on the lone pair of electrons on the N atom varies as α-picoline > β-picoline > γ-picoline, it follows that β-picoline–β-picoline and γ-picoline–γ-picoline solute–solute interactions should be more repulsive than α-picoline–α-picoline in the presence of pyridine. This is indeed true as is evident from the V_{BB} value for β-picoline and also for γ-picoline. If another α-picoline molecule now approaches the two α-picoline molecules which are assumed to be interacting as shown above, it is apparent that the net effect would now be attractive and this is reflected in the negative value of V_{BBB} for α-picoline–α-picoline–α-picoline interactions in the presence of pyridine. This is also true of the V_{BBB} values for β-picoline and γ-picoline in the presence of pyridine. Similar arguments also apply to the V_{BB} and V_{BBB} values of toluene, o-xylene and p-xylene in the presence of benzene. The negative V_{BBB} value for n-heptane in the presence of carbon tetrachloride may then be attractive n-heptane–n-heptane–n-heptane interaction due to van der Waals interactions.

V^E data for all these mixtures were then analysed in terms of the "graph theoretical approach" V^E according to this approach is given by [4]

$$V^E = \alpha_{ij}\left[\frac{1}{\sum x_i{}^3\xi_i} - \sum \frac{x_i}{{}^3\xi_i}\right] \tag{7}$$

where α_{ij} is a constant characteristic of the $(i+j)$ mixture. This approach is based on the fact that the molar volumes of aromatic hydrocarbons, alkanes and substituted alkanes at any temperature can be well described [4] by

$$V_i = \frac{\alpha_i}{{}^3\xi_i} + \beta_i{}^1\xi_i + \gamma_i \tag{8}$$

where α_i, β_i and γ_i are constants and ${}^1\xi_i$ is the connectivity parameter of the first degree of i.

Since pyridine, α-, β- and γ-picolines undergo reactions that are characteristic of the aromatic ring (disregarding, however, the basic nature of pyridine or the picolines for the present analysis), we expect that their molar volumes should almost be the same as that of the aromatic hydrocarbons. In actual fact, the molar volumes of pyridine, α-, β- or γ-picoline are almost 10% lower than that of benzene or toluene. Consequently, the molar volumes of pyridine, α-, β- or γ-picoline should also be expressible by eqn. (8) so that the V^E for all the present mixtures would be given by eqn. (2).

Evaluation of V^E according to this approach requires a knowledge of α_{ij} for the $(i+j)$ mixture and for the present analysis was evaluated by fitting V^E for an equimolar mixture to eqn. (7). This value of α_{ij} was then utilized to evaluate V^E for the mixture at that temperature and at any other composition. (The ${}^3\xi$ for the various components were taken from an earlier publication [4], while those for pyridine and α-, β- and γ-picoline were assumed to be the same as that for benzene and toluene, respectively). Such V^E values at $x_i = 0.1$, 0.3, 0.7 and 0.9 at 308.15 K are recorded in Table 4 and are also compared with their corresponding experimental values.

Examination of Table 4 reveals that eqn. (2) describes well the V^E data at 308.15 K for all these mixtures. Since the molar volume $V_i(T_1)$ of an i molecule at a temperature T_1 varies directly as T_1, it follows that

$$V_i(T_2) = \frac{T_2}{T_1} V_i(T_1) \tag{9}$$

$$= \frac{T_2}{T_1}\left[\frac{\alpha_i}{{}^3\xi_i} + \beta_i{}^1\xi_i + \gamma_i\right] \tag{10}$$

Consequently, if $V^E(T_1)$ represents the molar excess volume of an $(i+j)$ mixture at T_1 and at a given x_i and $V^E(T_2)$ is the molar excess volume for the same mixture at T_2 then

$$V^E(T_2) = V^E(T_1)\frac{T_2}{T_1} \tag{11}$$

TABLE 4

Comparison of V^E values measured at $T_1 = 308.15$ K with the corresponding V^E values calculated from eqn. (8) for the various binary mixtures at $x_1 = 0.1$, 0.3, 0.7 and 0.9

Mixture		V^E (cm^3 mole^{-1})			
		$x_1 = 0.1$	$x_1 = 0.3$	$x_1 = 0.7$	$x_1 = 0.9$
Pyridine(*i*)+	Calcd.	0.012	0.028	0.031	0.014
α-picoline(*j*)	Exptl.	0.011	0.026	0.029	0.011
Pyridine(*i*)+	Calcd.	0.009	0.022	0.023	0.011
β-picoline(*j*)	Exptl.	0.012	0.024	0.024	0.011
Pyridine(*i*)+	Calcd.	0.013	0.030	0.031	0.015
γ-picoline(*j*)	Exptl.	0.013	0.033	0.029	0.013
Benzene(*i*)+	Calcd.	0.030	0.073	0.079	0.036
toluene(*j*)	Exptl.	0.030	0.074	0.074	0.030
Benzene(*i*)+	Calcd.	0.076	0.194	0.240	0.116
o-xylene(*j*)	Exptl.	0.080	0.195	0.225	0.100
Benzene(*i*)+	Calcd.	0.065	0.163	0.194	0.091
p-xylene(*j*)	Exptl.	0.065	0.160	0.180	0.090
Carbon tetra chloride(*i*)+	Calcd.	0.045	0.110	0.118	0.053
n-heptane(*j*)	Exptl.	0.045	0.110	0.120	0.055

TABLE 5

Comparison of V^E values calculated from eqn. (11) from V^E ($T_1 = 308.15$ K) with the corresponding experimental values at $x_1 = 0.1$, 0.3, 0.7 and 0.9 for the various binary mixtures

Mixture	T_2 (K)		V^E (cm^3 mole^{-1})			
			$x_1 = 0.1$	$x_1 = 0.3$	$x_1 = 0.7$	$x_1 = 0.9$
Pyridine(*i*)+	318.15	Calcd.	0.012	0.029	0.032	0.015
α-picoline(*j*)		Exptl.	0.050	0.140	0.112	0.050
Pyridine(*i*)+	318.15	Calcd.	0.009	0.023	0.023	0.011
β-picoline(*j*)		Exptl.	0.021	0.048	0.045	0.017
Pyridine(*i*)+	318.15	Calcd.	0.013	0.031	0.032	0.015
γ-picoline(*j*)		Exptl.	0.016	0.039	0.032	0.014
Benzene(*i*)+	298.15	Calcd.	0.029	0.071	0.077	0.035
toluene(*j*)		Exptl.	0.024	0.066	0.066	0.026
Benzene(*i*)+	298.15	Calcd.	0.073	0.187	0.231	0.113
o-xylene(*j*)		Exptl.	0.080	0.210	0.225	0.105
Benzene(*i*)+	298.15	Calcd.	0.063	0.158	0.187	0.088
p-xylene(*j*)		Exptl.	0.065	0.165	0.180	0.085
Carbon tetra chloride(*i*)+	298.15	Calcd.	0.043	0.106	0.114	0.052
n-heptane(*j*)		Exptl.	0.040	0.100	0.108	0.052

TABLE 6

Comparison of $V^E(T_2)$ values as calculated using eqn. (11) from $V^E(T_1)$ with the corresponding experimental values at $x_1 = 0.3$ and 0.7 for the various binary mixtures

Mixture	Temperature (K)			$V^E(T_2)$ (cm^3 mole^{-1})	
	T_1	T_2		$x_1 = 0.3$	$x_1 = 0.7$
Benzene(*i*)+methylene chloride(*j*)	298.15	288.15	Calcd.	0.229	0.199
			Exptl. [18]	0.247	0.242
		303.15	Calcd.	0.241	0.209
			Exptl. [19]	0.234	0.195
Benzene(*i*)+nitromethane(*j*)	303.15	308.15	Calcd.	0.191	0.168
			Exptl. [20]	0.201	0.155
		318.15	Calcd.	0.197	0.173
			Exptl. [21]	0.177	0.115
Benzene(*i*)+1,2-dichloroethane(*j*)	298.15	308.15	Calcd.	0.207	0.181
			Exptl. [22]	0.196	0.192
		318.15	Calcd.	0.213	0.187
			Exptl. [23]	0.160	0.156
Benzene(*i*)+*n*-pentane(*j*)	293.15	288.15	Calcd.	0.091	0.121
			Exptl. [24]	0.111	0.108
Benzene(*i*)+toluene(*j*)	298.15	308.15	Calcd.	0.066	0.082
			Exptl. [25]	0.060	0.070
		318.15	Calcd.	0.068	0.084
			Exptl. [25]	0.051	0.046
Toluene(*i*)+methylene chloride(*j*)	298.15	288.15	Calcd.	0.149	0.126
			Exptl. [18]	0.160	0.110
		303.15	Calcd.	0.157	0.132
			Exptl. [19]	0.162	0.109
Toluene(*i*)+nitromethane(*j*)	303.15	308.15	Calcd.	0.153	0.121
			Exptl. [20]	0.159	0.082
		318.15	Calcd.	0.158	0.125
			Exptl. [21]	0.178	0.105
Toluene(*i*)+1,2-dichloromethane(*j*)	298.15	303.15	Calcd.	0.157	0.125
			Exptl. [22]	0.162	0.126
		318.15	Calcd.	0.162	0.129
			Exptl. [23]	0.176	0.138
Toluene(*i*)+*n*-pentane(*j*)	293.15	288.15	Calcd.	−0.216	−0.222
			Exptl. [24]	−0.269	−0.240
Toluene(*i*)+chlorobenzene(*j*)	298.15	308.15	Calcd.	−0.094	−0.088
			Exptl. [25]	−0.086	−0.080
		318.15	Calcd.	−0.104	−0.097
			Exptl. [25]	−0.080	−0.083
Toluene(*i*)+bromobenzene(*j*)	298.15	308.15	Calcd.	−0.102	−0.094
			Exptl. [25]	−0.121	−0.116
		318.15	Calcd.	−0.112	−0.104
			Exptl. [25]	−0.130	−0.125
o-Xylene(*i*)+methylene chloride(*j*)	298.15	288.15	Calcd.	0.216	0.152
			Expt. [18]	0.210	0.158

TABLE 6 (continued)

Mixture	Temperature (K)			$V^E(T_2)$ (cm^3 $mole^{-1}$)	
	T_1	T_2		$x_1 = 0.3$	$x_1 = 0.7$
		303.15	Calcd.	0.228	0.160
			Exptl. [19]	0.211	0.158
o-Xylene(*i*)+ nitromethane(*j*)	303.15	308.15	Calcd.	0.271	0.177
			Exptl. [20]	0.267	0.147
		318.15	Calcd.	0.280	0.183
			Exptl. [21]	0.303	0.217
o-Xylene(*i*)+1,2-dichloroethane(*j*)	298.15	303.15	Calcd.	0.215	0.307
			Exptl. [22]	0.285	0.227
		318.15	Calcd.	0.222	0.317
			Exptl. [23]	0.261	0.199
o-Xylene(*i*)+ *n*-pentane(*j*)	293.15	288.15	Calcd.	−0.452	−0.721
			Exptl. [24]	−0.551	−0.496
o-Xylene(*i*)+chlorobenzene(*j*)	298.15	293.15	Calcd.	−0.020	−0.016
			Exptl. [26]	−0.018	−0.022
		308.15	Calcd.	−0.021	−0.017
			Exptl. [27]	−0.040	−0.048
o-Xylene(*i*)+ bromobenzene(*j*)	298.15	293.15	Calcd.	−0.047	−0.037
			Exptl. [26]	−0.037	−0.037
		308.15	Calcd.	−0.050	−0.039
			Exptl. [27]	−0.056	−0.056
m-Xylene(*i*)+ methylene chloride(*j*)	298.15	288.15	Calcd.	0.324	0.241
			Exptl. [18]	0.323	0.238
		303.15	Calcd.	0.341	0.253
			Exptl. [19]	0.319	0.243
m-Xylene(*i*)+nitromethane(*j*)	303.15	308.15	Calcd.	0.274	0.203
			Exptl. [20]	0.295	0.170
		318.15	Calcd.	0.283	0.210
			Exptl. [21]	0.307	0.236
m-Xylene(*i*)+ 1,2- -dichloromethane(*j*)	298.15	303.15	Calcd.	0.344	0.271
			Exptl. [22]	0.346	0.244
		318.15	Calcd.	0.355	0.280
			Exptl. [23]	0.337	0.247
m-Xylene(*i*)+ *n*-pentane(*j*)	293.15	288.15	Calcd.	−0.350	−0.531
			Exptl. [24]	−0.390	−0.358
m-Xylene(*i*)+bromobenzene(*j*)	298.15	293.15	Calcd.	−0.071	−0.063
			Exptl. [26]	−0.047	−0.050
		308.15	Calcd.	−0.074	−0.066
			Exptl. [27]	−0.083	−0.090
p-Xylene(*i*)+methylene chloride(*j*)	298.15	288.15	Calcd.	0.222	0.161
			Exptl. [18]	0.228	0.161
		303.15	Calcd.	0.234	0.170
			Exptl. [19]	0.228	0.161
p-Xylene(*i*)+ nitromethane(*j*)	303.15	308.15	Calcd.	0.227	0.167
			Exptl. [20]	0.257	0.154

TABLE 6 (continued)

Mixture	Temperature (K)			$V^E(T_2)$ (cm^3 mole^{-1})	
	T_1	T_2		$x_1 = 0.3$	$x_1 = 0.7$
		318.15	Calcd.	0.234	0.172
			Exptl. [21]	0.273	0.206
p-Xylene(i)+1,2-dichloromethane(j)	298.15	303.15	Calcd.	0.259	0.189
			Exptl. [22]	0.261	0.196
		318.15	Calcd.	0.268	0.195
			Exptl. [23]	0.274	0.201
p-Xylene(i)+*n*-pentane(j)	293.15	288.15	Calcd.	−0.362	−0.556
			Exptl. [24]	−0.437	−0.410
p-Xylene(i)+chloro benzene(j)	298.15	293.15	Calcd.	−0.064	−0.052
			Exptl. [26]	−0.052	−0.058
		308.15	Calcd.	−0.067	−0.055
			Exptl. [27]	−0.071	−0.081
Cyclopentane(i)+2,3-dimethylbutane(j)	288.15	298.15	Calcd.	−0.232	−0.235
			Exptl. [28]	−0.225	−0.227
		313.15	Calcd.	−0.245	−0.247
			Exptl. [28]	−0.223	−0.227
Cyclohexane(i)+ methylene chloride(j)	298.15	288.15	Calcd.	0.822	0.714
			Exptl. [18]	0.817	0.805
		303.15	Calcd.	0.867	0.751
			Exptl. [19]	0.817	0.805
Cyclohexane(i)+ cyclopentane(j)	298.15	288.15	Calcd.	0.034	0.033
			Exptl. [29]	0.041	0.052
		308.15	Calcd.	0.036	0.035
			Exptl. [29]	0.016	0.026
Cyclohexane(i)+2,3--dimethylpentane(j)	288.15	298.15	Calcd.	−0.085	−0.088
			Exptl. [30]	−0.097	−0.097
		313.15	Calcd.	−0.089	−0.092
			Exptl. [30]	−0.112	−0.109
Cycloheptane(i)+2,3-dimethylbutane(j)	288.15	298.15	Calcd.	−0.361	−0.318
			Exptl. [31]	−0.392	−0.342
		313.15	Calcd.	−0.379	−0.334
			Exptl. [31]	−0.475	−0.414
Cyclooctane(i)+2,3--dimethylbutane(j)	288.15	298.15	Calcd.	−0.589	−0.502
			Exptl. [32]	−0.570	−0.536
		313.15	Calcd.	−0.619	−0.527
			Exptl. [32]	−0.755	−0.636
Cyclooctane(i)+ cyclopentane(j)	298.15	288.15	Calcd.	−0.253	−0.210
			Exptl. [33]	−0.235	−0.164
		308.15	Calcd.	−0.271	−0.224
			Exptl. [33]	−0.315	−0.239
Cyclooctane(i)+ cyclohexane(j)	298.15	288.15	Calcd.	−0.105	−0.078
			Exptl. [34]	−0.108	−0.080
		318.15	Calcd.	−0.116	−0.101
			Exptl. [34]	−0.117	−0.084

Equation (11) can thus be utilized to evaluate V^E for the mixture at any other temperature, T_2, when the V^E data for the same mixture at a given temperature, T_1, is known. Such $V^E(T_2)$ values for the various mixtures obtained from the $V^E(T_1)$ at $x_i = 0.1$, 0.3, 0.7 and 0.9 and at T_1 [calculated from a single V^E datum at $x_1 = 0.5$ at T_1 by means of eqn. (7)] are recorded in Table 5 and are also compared with the corresponding experimental values.

Examination of Table 5 reveals that, while the V^E values so evaluated compare very well with the corresponding experimental values for pyridine + γ-picoline, benzene + toluene, + *o*-xylene and + *p*-xylene mixtures, the same is not true of the V^E values for pyridine + α-picoline and + β-picoline mixtures; the calculated V^E values for the latter mixtures are consistently smaller than the corresponding experimental values.

In order to ascertain whether the failure of this approach for pyridine + α-picoline and + β-picoline is due to an insufficiency in this approach or whether some other kinds of interaction also come into play in them at higher temperatures, we checked the conclusions of eqn. (11) for a number of other binary mixtures of non-electrolytes, some of which are known to be characterized by the presence of weak specific interactions between their components. Examination of Table 6 clearly shows that eqn. (11) describes reasonably well the V^E data for a number of binary mixtures of non-electrolytes even when there are weak specific interactions between their components. The failure of this approach for pyridine + α-picoline and + β-picoline is thus due to the influence of some other kind of repulsive interactions.

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