Thermochimica Acta, 114 (1987) 337–346
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MOLAR EXCESS VOLUMES OF BINARY MIXTURES OF ETHYLBENZENE WITH n-ALKANES AT 298.15 K; AN INTERPRETATION IN TERMS OF THE PRIGOGINE–FLORY–PATTERSON MODEL

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(Received 4 September 1986)

ABSTRACT

Molar excess volumes are reported for binary mixtures of ethylbenzene with n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-dodecane, n-tetradecane and n-hexadecane at 298.15 K and over the whole mole fraction range. The Prigogine–Flory–Patterson model of solution thermodynamics has been used to predict the molar excess volumes. The values of V_m^E are well predicted and the results show the importance of the three contributions, ΔV_{inter}, ΔV_{P^*} and ΔV_F, to V_m^E.

INTRODUCTION

Molar excess volumes of binary mixtures of hydrocarbons have been studied extensively, both from theoretical and experimental points of view [1–5]. n-Alkane systems show a short-range orientational order phenomena which lead to an important contribution to the excess thermodynamic properties. The molar excess volume [6], molar excess enthalpy [7] and excess heat capacity [8] of some n-alkane and ethylbenzene systems have been reported. Molar excess enthalpies for ethylbenzene systems are found to be much smaller than those for benzene systems, which are similar to those of toluene systems [7]. Analysis of H^E data in terms of the Prigogine–Flory–Patterson model explained the difference in terms of the existence of order correlations between benzene molecules, which are absent in toluene and ethylbenzene molecules.

Recently, molar excess volumes were reported for binary mixtures of n-alkanes with benzene [9] and with toluene [10], and the V_m^E data were analysed in terms of the Prigogine–Flory–Patterson model. The analysis

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showed the importance of the three contributions ΔV_F, ΔV_{P^*}, and ΔV_{inter} to V_m^E. As a continuation of these investigations, we extend this work to n-alkanes and ethylbenzene systems to study the effect of the side chain in the aromatic ring on the molar excess volume. The present paper reports the molar excess volumes of the binary mixtures of ethylbenzene and n-alkanes: n-hexane (n-C_6), n-heptane (n-C_7), n-octane (n-C_8), n-nonane (n-C_9), n-decane (n-C_{10}), n-dodecane (n-C_{12}), n-tetradecane (n-C_{14}) and n-hexadecane (n-C_{16}). The V_m^E data obtained were analysed in terms of the Prigogine–Flory–Patterson model.

EXPERIMENTAL

Materials

The n-alkanes (Fluka AG, Puriss, P.a.) were used without further purification. All samples were stored over freshly activated 4A molecular sieve (Union Carbide) before use. Ethylbenzene (Fluka AG, Puriss grade) was purified by distillation at atmospheric pressure through a Vigreax column and then passed through an aluminium oxide column. The purified liquid was stored over sodium wire. The purity of the materials was checked by means of analytical GLC and density measurements. The densities at 298.15 K of the samples used in this study are listed in Table 1, together with the literature values for comparison.

Apparatus

The molar excess volumes V_m^E of the present systems were obtained from density data measured at 298.15 ± 0.001 K using a precision digital densime-

TABLE 1

Densities of pure component liquids at 298.15 K

Component	ρ (obs) (g cm^{-3})	ρ (lit) [a] (g cm^{-3})
Ethylbenzene	0.86249	0.86264
n-Hexane	0.65485	0.65481
n-Heptane	0.67966	0.67951
n-Octane	0.69876	0.69849
n-Nonane	0.71356	0.71381
n-Decane	0.72641	0.72625
n-Dodecane	0.74633	0.74516
n-Tetradecane	0.75933	0.75930
n-Hexadecane	0.76992	0.76996

[a] Ref. 11.

ter (Anton Paar, Model DMA 602). The estimated precision in the density measurements is better than 4×10^{-6} g cm^{-3}. The binary mixtures of ethylbenzene and n-alkanes were prepared on a mass basis. The error in the mole fractions of mixtures prepared is found to be less than 4×10^{-5}.

TABLE 2

Experimental molar excess volume for x ethylbenzene + $(1-x)$ n-alkanes at 298.15 K

x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})
x Ethylbenzene + $(1-x)$ n-hexane			
0.94878	−0.0292	0.43899	−0.1289
0.87566	−0.0650	0.40871	−0.1207
0.84784	−0.0791	0.36754	−0.1100
0.75049	−0.1201	0.31180	−0.0930
0.69005	−0.1368	0.26897	−0.0794
0.64759	−0.1439	0.22638	−0.0658
0.60929	−0.1489	0.17556	−0.0500
0.55323	−0.1465	0.06327	−0.0178
0.50860	−0.1416	0.03840	−0.0117
0.47664	−0.1367	0.01836	−0.0052
x Ethylbenzene + $(1-x)$ n-heptane			
0.94754	0.0157	0.48324	0.0560
0.89909	0.0204	0.45954	0.0604
0.85014	0.0322	0.41089	0.0597
0.80116	0.0331	0.36834	0.0575
0.76969	0.0404	0.30212	0.0508
0.71495	0.0451	0.26654	0.0455
0.68769	0.0474	0.20322	0.0338
0.64444	0.0508	0.18911	0.0309
0.60009	0.0541	0.13543	0.0194
0.54633	0.0575	0.10933	0.0140
0.51811	0.0588	0.06996	0.0068
0.49804	0.0596	0.02356	0.0010
x Ethylbenzene + $(1-x)$ n-octane			
0.96783	0.0261	0.42503	0.2240
0.90763	0.0617	0.36653	0.2111
0.86864	0.0879	0.31109	0.1924
0.82340	0.1172	0.29060	0.1841
0.75633	0.1563	0.25959	0.1699
0.70437	0.1819	0.20465	0.1411
0.63611	0.2078	0.14834	0.1069
0.59323	0.2192	0.10399	0.0771
0.55302	0.2261	0.07735	0.0583
0.51137	0.2295	0.04989	0.0381
0.49712	0.2297	0.01570	0.0122
0.45600	0.2279		

TABLE 2 (continued)

x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})
x Ethylbenzene + $(1-x)$ n-nonane			
0.91120	0.1050	0.49441	0.3099
0.86388	0.1627	0.46388	0.3093
0.84304	0.1856	0.43922	0.3079
0.78652	0.2369	0.40397	0.3043
0.74389	0.2646	0.36874	0.2995
0.71220	0.2796	0.32218	0.2675
0.68734	0.2886	0.28984	0.2557
0.63214	0.3014	0.25502	0.2271
0.61988	0.3032	0.20299	0.1875
0.58994	0.3065	0.16854	0.1552
0.55233	0.3089	0.10333	0.0894
0.51305	0.3099	0.05705	0.0371
x Ethylbenzene + $(1-x)$ n-decane			
0.94343	0.0741	0.44323	0.3835
0.89790	0.1340	0.40783	0.3739
0.84989	0.1942	0.36312	0.3631
0.78128	0.2697	0.31979	0.3267
0.73998	0.3080	0.27452	0.2933
0.70951	0.3319	0.23940	0.2625
0.64217	0.3742	0.17837	0.2175
0.58978	0.3890	0.11568	0.1526
0.52480	0.3961	0.06009	0.0859
0.47976	0.3919	0.02276	0.0345
x Ethylbenzene + $(1-x)$ n-dodecane			
0.97687	0.0567	0.42734	0.4352
0.90647	0.1999	0.36725	0.3954
0.82945	0.3116	0.31739	0.3647
0.77954	0.3666	0.25846	0.3131
0.73830	0.4008	0.19979	0.2492
0.68734	0.4330	0.13392	0.1706
0.65837	0.4660	0.07764	0.0990
0.58773	0.4637	0.04899	0.0794
0.54304	0.4650	0.01774	0.0177
0.47615	0.4590		
x Ethylbenzene + $(1-x)$ n-tetradecane			
0.97853	0.0663	0.43000	0.5036
0.91548	0.2303	0.38269	0.4728
0.87533	0.3125	0.32998	0.4304
0.84235	0.3692	0.29491	0.3973
0.80115	0.4272	0.25018	0.3514
0.76152	0.4689	0.21976	0.3168
0.73939	0.4906	0.16478	0.2485
0.69094	0.5247	0.13754	0.2116
0.64989	0.5460	0.09734	0.1541
0.58612	0.5514	0.05192	0.0848
0.53939	0.5460	0.02009	0.0368
0.48520	0.5298		

TABLE 2 (continued)

x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})
x Ethylbenzene + (1 − x) n-hexadecane			
0.94544	0.1964	0.43023	0.5301
0.90807	0.2989	0.39978	0.5125
0.86231	0.3905	0.34945	0.4735
0.81079	0.4692	0.28740	0.4123
0.78596	0.4968	0.24755	0.3658
0.73994	0.5353	0.20115	0.3048
0.67086	0.5685	0.15539	0.2386
0.64956	0.5739	0.10489	0.1607
0.60452	0.5818	0.08732	0.1331
0.53945	0.5737	0.05956	0.0894
0.48754	0.5588	0.01992	0.0288

RESULTS AND DISCUSSION

The experimental V_m^E results obtained from precise density measurements at 298.15 ± 0.001 K are listed in Table 2. Each set of V_m^E data was fitted to the following equation by the least-squares method.

$$V_m^E(\mathrm{cm^3\ mol^{-1}}) = x(1-x)\sum_{j=1}^{n} a_j(1-2x)^{j-1} \tag{1}$$

The values of the coefficients a_j are listed in Table 3 together with the standard deviation, σV_m^E, of fits, which is evaluated from the equation:

$$\sigma V_m^E = \left[\frac{(\Delta V^E)^2}{n-p}\right]^{1/2} \tag{2}$$

where n is the number of experimental points and p is the number of coefficients in eqn. (1).

TABLE 3

Coefficients a_j and standard deviations σV^E of eqn. (1)

System	a_1	a_2	a_3	a_4	$10^{-5}\ \sigma V^E$
Ethylbenzene +					
n-Hexane	−0.5586	−0.2908	0.1529	0.1652	9
n-Heptane	0.2374	−0.0694	−0.0609	0.8339	8
n-Octane	0.9091	−0.0548	−0.1505	0.0517	10
n-Nonane	1.2440	0.1101	0.5142	0.2519	2
n-Decane	1.5827	0.2087	−0.1656	−0.3631	10
n-Dodecane	1.8403	0.3809	0.0749	0.2857	5
n-Tetradecane	2.1336	0.7096	0.3569		2
n-Hexadecane	2.2528	0.6656	0.5568	0.7356	3

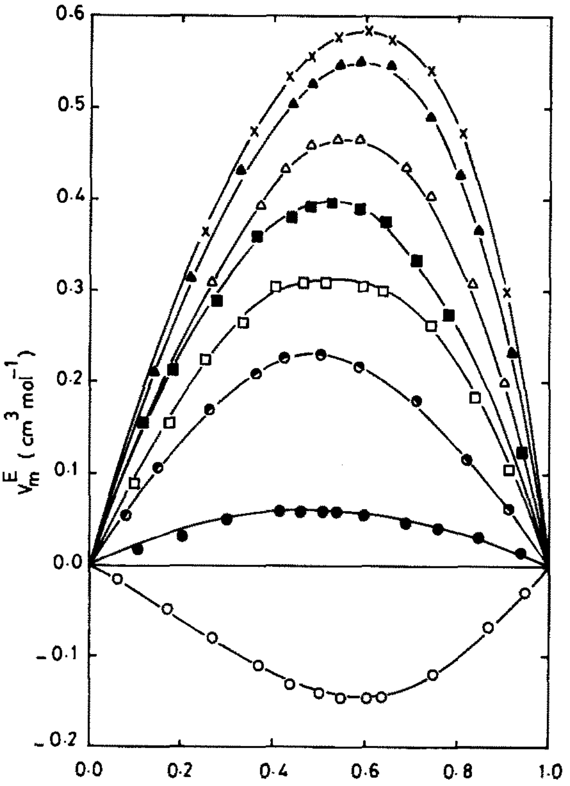

Fig. 1. Molar excess volumes of x ethylbenzene + $(1-x)$ n-alkanes at 298.15 K. (○) n-C_6; (●) n-C_7; (◒) n-C_8; (□) n-C_9; (■) n-C_{10}; (△) n-C_{12}; (▲) n-C_{14}; (×) n-C_{16}.

The experimental molar excess volume is negative for ethylbenzene + n-hexane and positive for ethylbenzene + n-heptane, + n-octane, + n-nonane, + n-decane, + n-dodecane, + n-tetradecane and + n-hexadecane over the whole mole fraction range at 298.15 K (Fig. 1). The V_m^E results obtained here for this class of mixtures are found to be in reasonable agreement with values published in the literature [6]. For example, at $x = 0.5$ and 298.15 K, the V_m^E values for ethylbenzene + n-heptane, + n-decane, + n-dodecane and + n-tetradecane are 0.0595, 0.3557, 0.4462 and 0.4930, while ours are 0.0593, 0.3957, 0.4601 and 0.5334, respectively. It is apparent that the magnitude of V_m^E for the ethylbenzene system is similar to that for toluene [10] and much smaller than that for benzene system [9]. The maximum value, for the ethylbenzene + n-hexadecane system is 0.581 cm^3 mol^{-1} ($x = 0.395$), for the toluene system is 0.562 cm^3 mol^{-1} ($x = 0.380$), and for the benzene system is 1.250 cm^3 mol^{-1} ($x = 0.434$) (x is the mole fraction of n-alkanes). It seems that the sequence of V_m^E is consistent with that for H^E.

TABLE 4

Equation of state parameters for the pure component liquids at 298.15 K

Component	V [a] (cm^3 mol^{-1})	$10^3\alpha$ (K^{-1})	P^* (J cm^{-3})	V^* (cm^3 mol^{-1})	T^* (K)
Ethylbenzene	123.12	1.016 [b]	533 [c]	98.42	5231
n-Hexane	131.61	1.391 [d]	423 [d]	99.50	4430
n-Heptane	147.48	1.235 [d]	432 [d]	123.67	4653
n-Octane	163.59	1.165 [d]	439 [d]	127.70	4825
n-Nonane	179.65	1.077 [d]	435 [d]	142.21	5025
n-Decane	195.94	1.050 [d]	448 [d]	155.76	5094
n-Dodecane	228.53	0.980 [d]	455 [d]	183.77	5290
n-Tetradecane	261.27	0.921 [d]	460 [d]	212.19	5479
n-Hexadecane	294.09	0.884 [d]	463 [d]	240.39	5611

[a] This work. [b] From density measurements. [c] From compressibility data in ref. 12. [d] Ref. 13.

Molar excess volumes of ethylbenzene and n-alkanes systems were analysed in terms of the Prigogine–Flory–Patterson model, using the pure component parameters and X_{12} (Tables 4 and 5) [2]:

$$\frac{V^{\mathrm{E}}}{x_1V_1^* + x_2V_2^*} = \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}}{(4/3\tilde{V}^{-1/3}-1)}\psi_1\theta_2\frac{X_{12}}{P_1^*} - \frac{(\tilde{V}_1-\tilde{V}_2)^2(14/9\tilde{V}^{-1/3}-1)}{(4/3\tilde{V}^{-1/3}-1)\tilde{V}}\psi_1\psi_2 + \frac{(\tilde{V}_1-\tilde{V}_2)(P_1^*-P_2^*)}{P_2^*\psi_1+P_1^*\psi_2}\psi_1\psi_2 \qquad (3)$$

The first term is the interactional contribution to $V_{\mathrm{m}}^{\mathrm{E}}(\Delta V_{\mathrm{inter}})$, the second one is the free volume difference contribution (ΔV_{F}), and the third one is the internal pressure contribution (ΔV_{p^*}).

The theoretical $V_{\mathrm{m}}^{\mathrm{E}}$ values and the three contributions (ΔV_{F}, ΔV_{p^*} and $\Delta V_{\mathrm{inter}}$) to $V_{\mathrm{m}}^{\mathrm{E}}$ obtained from eqn. (3) are listed in Table 5 and illustrated in Fig. 2. The total theoretical $V_{\mathrm{m}}^{\mathrm{E}}$ values are found to be in excellent agreement with experimental ones (Table 5).

The interactional contribution, $\Delta V_{\mathrm{inter}}$, is large and positive (Table 5) and its magnitude for the ethylbenzene system is similar to that for toluene [10] and half that for the benzene system [9]. For example, $\Delta V_{\mathrm{inter}}$ for the ethylbenzene + n-hexadecane system is 0.433, for the toluene + n-hexadecane system is 0.460 [10], and for the benzene + n-hexadecane system is 0.982 [9]. This is the same as the sequence of H^{E} data used in the calculation of X_{12} in the first term of eqn. (3).

The internal pressure contribution (ΔV_{p^*}) is negative for lower n-alkanes $(\tilde{V}_1 < \tilde{V}_2)$ and positive for higher n-alkanes ($P_1^* > P_2^*$ and $\tilde{V}_1 > \tilde{V}_2$). The absence of V_{p^*} leads to a large change in the total $V_{\mathrm{m}}^{\mathrm{E}}$; for example, for the ethylbenzene + n-hexadecane system, $V_{\mathrm{m}}^{\mathrm{E}}$ would be 0.391 cm^3 mol^{-1}.

TABLE 5

Experimental and theoretical molar excess volumes (cm^3 mol^{-1}) of ethylbenzene (1) + n-alkanes (2) at 298.15 K

System	X_{12} ($J\ cm^{-3}$)	ΔV_F	ΔV_{P^*}	ΔV_{inter}	V^E_{theor}	V^E_{exp}
Ethylbenzene (1) +						
n-Hexane (2)	15.6 [a]	−0.187	−0.409	0.385	−0.207	−0.139
n-Heptane (2)	15.7 [a]	−0.085	−0.258	0.375	0.032	0.059
n-Octane (2)	15.8 [b]	−0.037	−0.160	0.384	0.187	0.227
n-Nonane (2)	15.8 [a]	−0.007	−0.074	0.380	0.299	0.311
n-Decane (2)	15.9 [b]	−0.002	−0.037	0.396	0.357	0.395
n-Dodecane (2)	16.5 [b]	−0.003	0.037	0.402	0.437	0.460
n-Tetradecane (2)	16.9 [b]	−0.041	0.099	0.412	0.470	0.533
n-Hexadecane (2)	17.9 [b]	−0.042	0.139	0.433	0.530	0.563

[a] Estimated. [b] Ref. 7.

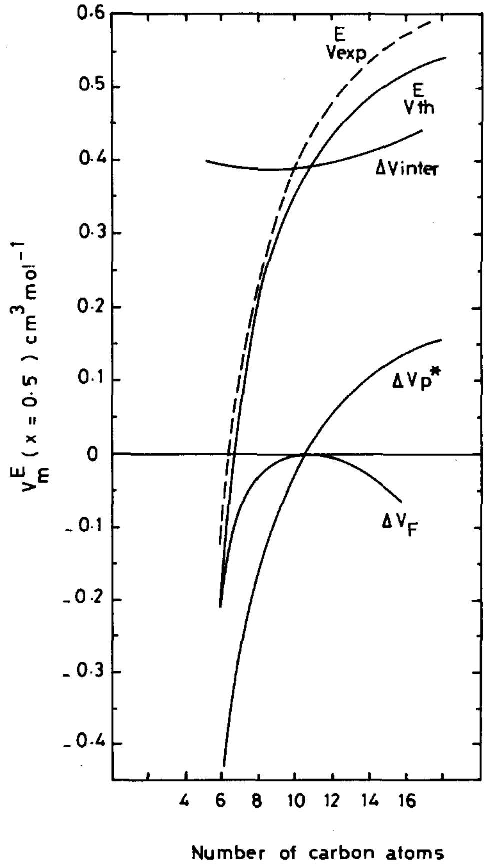

Fig. 2. Experimental and theoretical V^E_m at $x = 0.5$ and 298.15 K. The three contributions to V^E_m, ΔV_{inter}, ΔV_{P^*} and ΔV_F, are indicated.

The free volume difference contribution (ΔV_F) is negative for all systems studied. This contribution is more important for lower n-alkanes than for longer n-alkanes. For example the total V_m^E for the ethylbenzene + n-hexane system would be 0.024 cm^3 mol^{-1} and for the ethylbenzene + n-hexadecane would be 0.572 cm^3 mol^{-1} (see Table 5 for total V_m^E).

The values of V_m^E for ethylbenzene systems are nearly the same as that for the toluene system and are nearly half of the corresponding values for benzene systems. Such behaviour is probably due to: (i) the $P_1^\star$ and $\tilde{V}_1$ values for benzene being much larger than for toluene or ethylbenzene and (ii) the molecular order contribution in benzene molecules, which is absent in toluene and ethylbenzene.

LIST OF SYMBOLS

a_j	coefficient in eqn. (1)
H^E	excess enthalpy
n	number of experimental points in eqn. (1)
p	number of coefficients in eqn. (1)
$P_i^\star$	characteristic pressure of pure component
$T_i^\star$	characteristic temperature of pure component
V_i	molar volume of pure component
$V_j^\star$	characteristic volume of pure component
$\tilde{V}$	reduced volume of mixture
V_m^E	molar excess volume
ΔV_{inter}	the interactional contribution to V_m^E
ΔV_F	the free volume difference contribution to V_m^E
$\Delta V_{P^\star}$	the $P^\star$ contribution to V_m^E
x	mole fraction of ethylbenzene
X_{12}	interchange interaction parameter in Flory theory

Greek letters

α	thermal expansion coefficient
σ	standard deviation
ψ_i	energy fraction
θ_i	contact surface fraction
ρ	density of the pure component

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