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Excess Volumes of Binary Liquid Mixtures. Methyl Ethyl Ketone + Benzene, + Toluene, + Chlorobenzene, + Bromobenzene, and + Nitrobenzene at 303.15 and 313.15 K

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Excess volumes for the binary mixtures of methyl ethyl ketone with benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene have been determined at 303.15 and 313.15 K. V^E values are negative over the entire range of composition for all the systems and at both temperatures. The data are examined in terms of Flory's original theory. A sign agreement is found for the systems containing polar-polar components which fails in the case of polar-nonpolar systems. Flory's modified method predicted a sign agreement in V^E and H^E for the system methyl ethyl ketone + benzene.

As a part of our study on thermodynamic properties of binary liquid mixtures and applicability of the Flory theory (*1*, *2*) we examined excess volumes of five binary mixtures in terms of the Flory theory (*3*, *4*). V^E for the mixtures of methyl ethyl ketone (MEK) with benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene has been measured at 303.15 and 313.15 K. These systems were selected to study the effect of substitution of various groups on the benzene ring on the molecular interaction in the presence of a polar component. A literature survey has shown that the excess volumes for these systems have not been reported except for the methyl ethyl ketone + benzene system by using density measurement (*5*).

Experimental Section

Excess volumes were measured by using a single composition per loading type dilatometer described earlier (*6*). V^E values were accurate to ±0.003 cm^3 mol^{-1}. All the chemials were analytical-grade commercial products. Methyl ethyl ketone (BDH), benzene (BDH), and toluene (BDH) were further purified by the methods described earlier (*1*, *6*). Chlorobenzene (BDH), bromobenzene (E. Merck), and nitrobenzene (BDH) were dried over calcium chloride and fractionally distilled. The middle portion of the distillate collected at constant boiling point was used for the experiment. The purity of the samples was checked by comparing the values of density and refractive index with those reported in the literature (*7*).

Results and Theory

Excess volumes of the five binary mixtures measured at 303.15 and 313.15 K are given in Table I. These results are represented by an empirical equation of the form

$$V^E = x_1x_2[V_0 + (x_1 - x_2)V_1 + (x_1 - x_2)^2V_2] \quad (1)$$

The parameters V_0, V_1, and V_2 and their standard deviations are obtained by the method of least squares and are given in Table II along with the standard deviation $\sigma(V^E)$. The difference between the experimental excess volumes and the values obtained from eq 1 are also included in Table I.

The necessary equations for prediction of excess volumes are given in our earlier paper (*1*) with their usual significance as described by Flory (*3*, *4*). The values of the parameters for pure components are given in Table III. The interaction parameter, X_{AB}, and V^E values predicted on the basis of Flory's original method are given in Table IV for all the systems at 0.5 mole fraction. The results of Flory's modified method are in-

Table I. Mole Fraction x_1 of Methyl Ethyl Ketone and Experimental Excess Volumes V^E and ΔV^E

303.15 K			313.15 K		
x_1	V^E/ (cm^3 mol^{-1})	ΔV^{Ea}/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	ΔV^{Ea}/ (cm^3 mol^{-1})
MEK (1) + C_6H_6 (2)					
0.1485	−0.069	+0.001	0.1753	−0.073	−0.004
0.2359	−0.108	−0.001	0.2819	−0.107	+0.005
0.3313	−0.141	−0.002	0.3575	−0.134	+0.003
0.4063	−0.156	−0.001	0.4610	−0.156	+0.002
0.5162	−0.161	+0.002	0.5232	−0.165	−0.004
0.6868	−0.138	−0.002	0.6077	−0.158	−0.003
0.8032	−0.091	+0.003	0.7321	−0.127	−0.003
0.8831	−0.059	−0.001	0.8453	−0.074	−0.002
MEK (1) + $C_6H_5CH_3$ (2)					
0.1849	−0.136	−0.002	0.1757	−0.112	−0.002
0.2614	−0.174	+0.002	0.2195	−0.135	+0.001
0.3535	−0.216	+0.000	0.3479	−0.192	+0.002
0.4318	−0.239	+0.000	0.4364	−0.221	+0.001
0.5153	−0.253	−0.001	0.5739	−0.242	−0.001
0.5406	−0.256	−0.003	0.6582	−0.233	−0.001
0.7122	−0.229	−0.003	0.7512	−0.205	−0.002
0.8178	−0.172	+0.001	0.8355	−0.154	+0.002
MEK (1) + C_6H_5Cl (2)					
0.1424	−0.151	+0.003	0.1645	−0.157	+0.000
0.1972	−0.205	+0.003	0.2318	−0.218	−0.001
0.3602	−0.291	+0.004	0.3441	−0.303	−0.002
0.4074	−0.322	+0.007	0.3656	−0.309	+0.004
0.5576	−0.355	+0.002	0.4461	−0.354	+0.000
0.6242	−0.362	−0.002	0.6179	−0.376	−0.002
0.7288	−0.337	+0.000	0.7419	−0.324	−0.003
0.8531	−0.249	−0.002	0.8406	−0.232	+0.001
MEK (1) + C_6H_5Br (2)					
0.1321	−0.142	−0.002	0.1458	−0.148	−0.003
0.1917	−0.202	+0.001	0.1956	−0.185	+0.004
0.2946	−0.297	+0.002	0.3898	−0.338	+0.001
0.4169	−0.381	−0.001	0.4447	−0.372	−0.001
0.5535	−0.405	+0.003	0.5619	−0.414	+0.002
0.6908	−0.364	−0.002	0.5891	−0.419	+0.002
0.7512	−0.321	−0.003	0.7234	−0.405	−0.004
0.8335	−0.231	+0.003	0.7637	−0.379	−0.003
			0.8697	−0.262	+0.002
MEK (1) + $C_6H_5NO_2$ (2)					
0.1671	−0.305	−0.001	0.1725	−0.336	+0.002
0.2178	−0.369	+0.002	0.2138	−0.388	+0.000
0.3186	−0.482	−0.002	0.3047	−0.474	+0.002
0.4282	−0.565	−0.002	0.3732	−0.536	−0.006
0.5321	−0.601	+0.005	0.4426	−0.584	−0.006
0.6752	−0.595	−0.003	0.5873	−0.645	+0.005
0.7508	−0.541	−0.002	0.7146	−0.644	+0.005
0.8161	−0.457	+0.001	0.8539	−0.498	−0.004

[a] $\Delta V^E = V^E(\text{exptl}) - V^E(\text{eq } 1)$.

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Table II. Standard Deviation, σ, and Values of the Parameters in Eq 1

system	T/K	V_0[a]	V_1[a]	V_2[a]	$\sigma(V^E)$[a]
MEK + C_6H_6	303.15	−0.6536 (±0.0011)	−0.0156 (±0.0014)	+0.1827 (±0.0036)	0.002
MEK + $C_6H_5CH_3$	303.15	−1.0030 (±0.0010)	−0.2152 (±0.0017)	−0.0483 (±0.0045)	0.002
MEK + C_6H_5Cl	303.15	−1.3834 (±0.0021)	−0.5023 (±0.0030)	−0.4632 (±0.0072)	0.004
MEK + C_6H_5Br	303.15	−1.6246 (±0.0018)	−0.3098 (±0.0022)	+0.3193 (±0.0059)	0.003
MEK + $C_6H_5NO_2$	303.15	−2.3882 (±0.0017)	−0.6925 (±0.0023)	−0.5750 (±0.0068)	0.003
MEK + C_6H_6	313.15	−0.6430 (±0.0021)	−0.0912 (±0.0033)	+0.2558 (±0.0083)	0.004
MEK + $C_6H_5CH_3$	313.15	−0.9414 (±0.0011)	−0.2853 (±0.0015)	−0.0082 (±0.0040)	0.002
MEK + C_6H_5Cl	313.15	−1.4839 (±0.0017)	−0.4471 (±0.0023)	+0.0948 (±0.0061)	0.003
MEK + C_6H_5Br	313.15	−1.5864 (±0.0015)	−0.7980 (±0.0021)	−0.2820 (±0.0042)	0.003
MEK + $C_6H_5NO_2$	313.15	−2.4460 (±0.0028)	−1.0901 (±0.0039)	−1.4871 (±0.0101)	0.005

[a] Units: $cm^3\ mol^{-1}$.

Table III. Flory Parameters of the Pure Components (*3, 4*)

component	$10^3\alpha$[a]$/deg^{-1}$	κ_T[b]$/TPa^{-1}$	$V/(cm^3\ mol^{-1})$	$\tilde{v}$	$V^*/(cm^3\ mol^{-1})$	$p^*/(J\ cm^{-3})$	$\tilde{T}$
			303.15 K				
C_6H_6	1.242	1007.0	89.81	1.299	69.12	623.4	0.064 32
$C_6H_5CH_3$	1.079	944.2	107.44	1.267	84.80	550.6	0.059 82
C_6H_5Cl	0.985	784.6	102.75	1.248	82.33	592.8	0.057 04
C_6H_5Br	0.896	686.4	105.98	1.229	86.24	597.7	0.054 05
$C_6H_5NO_2$	0.818	523.0	103.16	1.212	85.11	696.5	0.051 22
MEK	1.256	1110.8	90.77	1.302	69.72	581.1	0.064 64
			313.15 K				
C_6H_6	1.258	1085.2	91.08	1.309	69.58	622.3	0.065 57
$C_6H_5CH_3$	1.091	1009.8	108.61	1.277	85.05	551.6	0.061 39
C_6H_5Cl	1.005	844.3	103.76	1.259	82.41	590.8	0.058 69
C_6H_5Br	0.992	745.9	106.95	1.241	86.18	596.1	0.055 96
$C_6H_5NO_2$	0.865	598.1	104.01	1.229	84.63	720.4	0.054 05
MEK	1.271	1190.5	91.72	1.313	69.86	576.2	0.066 08

[a] Thermal expansion coefficient is calculated from measured precision density values for all the components. [b] Isothermal compressibility is obtained from measured sound velocity, density, and literature heat capacity (*7, 9*) values by using the relation $\kappa_T = \kappa_S + \alpha^2 TV/C_p$ for all the components.

Table IV. Experimental and Predicted Values of V^E Using Original Flory Theory at 0.5 Mole Fraction of Methyl Ethyl Ketone

T/K	$X_{AB}/(J\ cm^{-3})$	$V^E_{exptl}/(cm^3\ mol^{-1})$	$V^E_{Flory}/(cm^3\ mol^{-1})$
	MEK + C_6H_6		
303.15	0.682	−0.161	0.011
313.15	0.853	−0.164	0.006
	MEK + $C_6H_5CH_3$		
303.15	0.019	−0.253	0.033
313.15	0.073	−0.235	0.023
	MEK + C_6H_5Cl		
303.15	0.857	−0.343	−0.096
313.15	0.978	−0.368	−0.089
	MEK + C_6H_5Br		
303.15	1.499	−0.404	−0.181
313.15	1.645	−0.395	−0.176
	MEK + $C_6H_5NO_2$		
303.15	10.484	−0.592	−0.431
313.15	13.721	−0.614	−0.534

cluded in Table V for the system methylethyl ketone + benzene, for which experimental enthalpy data were available (*8*).

Discussion

Excess volumes given in Table I are negative for all the systems over the entire range of composition. The negative excess volumes follow the order benzene > toluene > chlorobenzene ≈ bromobenzene > nitrobenzene. This order is parallel to their dielectric constant values. The results are attributed to the induced dipole and dipole interaction between π electrons of the benzene ring and the ketoxy group of MEK in the systems MEK + benzene and + toluene. In addition to the above effect a dipole–dipole interaction between the groups >CO with Cl, Br, and NO_2 may be responsible for the large negative excess volumes observed in the other three systems. The effect of temperature is small in the interval of temperature studied; however, both negative and positive temperature coefficients are observed in these systems.

An examination of the results shown in Table IV indicates that the original Flory theory predicts the sign of excess volumes with respect to the systems methyl ethyl ketone + chlorobenzene, + bromobenzene, and + nitrobenzene but fails with respect to the systems methyl ethyl ketone + benzene and + toluene. The results given in Table V reveal that the modified Flory theory also predicts the sign agreement in V^E and H^E of the system methyl ethyl ketone + benzene. This supports the trend observed in our earlier paper for the system diethyl ketone, + benzene (*1*).

Glossary

H^E_{Flory}	Flory's excess enthalpy, $= x_A p_A^* V_A^* (\tilde{v}_A^{-1} - \tilde{v}^{-1}) + x_B p_B^* V_B^* (\tilde{v}_B^{-1} - \tilde{v}^{-1}) + x_A V_A^* \theta_B X_{AB} \tilde{v}^{-1}$
κ_T	isothermal compressibility
p^*	characteristic pressure, $= \alpha T \tilde{v}^2 \kappa_T^{-1}$

Table V. Experimental and Predicted Values of V^E and H^E for the System MEK (1) + C_6H_6 (2) Using Modified Flory Theory at 0.5 Mole Fraction

T/K	$X_{AB}(H^E)/(J\ cm^{-3})$	$V^E_{exptl}/(cm^3\ mol^{-1})$	$V^E_{Flory}/(cm^3\ mol^{-1})$	$X_{AB}(V^E)/(J\ cm^{-3})$	H^E_{exptl}[a]$/(J\ mol^{-1})$	$H^E_{Flory}/(J\ mol^{-1})$
303.15	−2.789	−0.161	−0.028	−11.586	−49.53	−211.44
313.15	−2.305	−0.164	−0.049	−10.476	−49.53	−195.67

[a] H^E values are at 298.15 K.

$\tilde{T}$	reduced temperature; $\tilde{T}_A = (\tilde{v}_A^{1/3} - 1)\tilde{v}_A^{-4/3}$
V^E	excess volume
V^E_{Flory}	Flory's excess volume, $=(x_AV_A^* + x_BV_B^*)(\tilde{T} - \tilde{T}^0)(\tilde{v}^0)^{7/3}/[^4/_3 - (\tilde{v}^0)^{1/3}]$
V	molar volume
$\tilde{v}$	reduced volume, $=[(1 + 4\alpha T/3)/(1 + \alpha T)]^3$
V^*	characteristic volume, $=V/\tilde{v}$
V_0, V_1, V_2	coefficients in eq 1
X_{AB}	interaction parameter, $=p_A^*[1 - (V_B^*/V_A^*)^{1/6}\cdot(p_B^*/p_A^*)^{1/2}]^2$
$X_{AB}(H^E)$	interaction parameter calculated from excess enthalpy
x_i	mole fraction of component i
α	thermal expansivity
σ	standard deviation

Registry No. Methyl ethyl ketone, 78-93-3; benzene, 71-43-2; toluene, 108-88-3; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; nitrobenzene, 98-95-3.

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Solubilities of Carbon Dioxide in Heavy Normal Paraffins (C_{20}–C_{44}) at Pressures to 9.6 MPa and Temperatures from 323 to 423 K

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Solubility data have been obtained for carbon dioxide in the heavy normal paraffin solvents *n*-eicosane, *n*-octacosane, *n*-hexatricontane, and *n*-tetratetracontane. Measurements were made over the temperature range from 323 to 423 K (122 to 302 °F) at pressures up to 9.6 MPa (1400 psia). At carbon dioxide mole fractions below 0.45, the solubility data are described by the Krichevsky–Kasarnovsky equation with average deviations of 0.002 in mole fraction.

Introduction

Vapor–liquid phase equilibrium data are an essential element in the rational design and development of many industrial processes as well as for the enhancement of our understanding of fluid-phase behavior. CO_2 + hydrocarbon vapor–liquid equilibria data, in particular, are of interest in a number of industrial processes, including processing of petroleum products, production of coal liquids, and enhanced oil recovery.

Limited data are available on systems involving CO_2 and those heavy normal paraffin solvents which are solid at room temperature. Only two studies have been found in the literature dealing with such systems. The first system is CO_2 + *n*-eicosane reported by Huie et al. (*1*), and the second is CO_2 with traces of *n*-octacosane presented recently by McHugh et al. (*2*).

The purpose of the investigation reported here was to obtain solubility data for CO_2 in the following members of the normal paraffin homologous series: *n*-eicosane (*n*-C_{20}), *n*-octacosane (*n*-C_{28}), *n*-hexatricontane (*n*-C_{36}), *n*-tetratetracontane (*n*-C_{44}). These studies were designed to provide useful information for the further development of generalized predictive methods, which thus far have necessarily been based on insufficient data for heavy paraffin molecules (see, e.g., ref *3*).

Experimental Method

The experimental apparatus and procedures used in this work are described in detail by Gasem (*4*) and are summarized briefly below. The general arrangement of the apparatus is illustrated in Figure 1. It employs a static-type equilibrium cell. One distinct feature of the apparatus is its capability for handling solvents which are solid at room temperature. Solvent solidification presents significant problems in conventional equilibrium apparatuses; this may explain, in part, the lack of data for such systems.

The central part of the apparatus is a high-pressure, variable-volume, rocking cell housed in a constant-temperature bath. The equilibrium cell (EC) is a 90-cm^3 high-pressure stainless steel cylinder held in an aluminum block rocking assembly. The effective volume of the cell can be varied by the introduction or withdrawal of mercury. The apparatus is designed specifically to accommodate heavy solvents (solids at room temperature) by placing the solvent reservoir (SV) inside the high-temperature air oven (TB). The reservoir is a 125-cm^3 commercial reactor bomb with screw-top closure, which may be filled with the solid solvent by removing the top of the bomb.

Injections of solvent (liquid at the operating temperatures) into the equilibrium cell are done volumetrically by injecting mercury at the bottom of the solvent cylinder, thus displacing an equal quantity of solvent into the rocking cell. Sequential injections of solute are then made in like fashion from the solute storage cylinder (SU). The solute is housed in an external constant-temperature bath (TR), so it may be injected as gas or liquid as desired. The injected volumes are metered from a precision screw pump (SP) maintained at room temperature.

After each injection of solute into the solvent in the rocking cell, the bubble point pressure of the mixture is determined. This is done by injecting known amounts of mercury into the cell to alter the system volume. After each mercury injection, the cell is rocked to bring the system to equilibrium and the pressure is recorded. The bubble point pressure is located by observing the break point in a pressure–volume curve as the system passes from a two-phase to an all-liquid condition; example plots are shown in Figure 2.

Prior to an experiment, the hydrocarbon solvent is thoroughly degassed by applying a vacuum to the solvent. This degassing procedure is initiated at room temperature while the solvent is