

Figure 7. Comparison for diffusion coefficients of CO₂ in binary mixtures between experimental results and calculated values from eq 4 with $n = 1/3$. Symbols are the same as those in Figure 6.

On the other hand, the diffusion coefficients of CO₂ in binary mixtures can be estimated by the same equation as in a previous paper (22), that is, eq 4 based on the activated state theory.

$$D_{Am}\mu_m^n = \sum x_i D_{Ai}\mu_i^n (v_m/v_i)^{(2/3)-n} \quad (4)$$

Then, the value of n in eq 4 was examined from the viscosity data (4).

Figure 7 shows the comparison between the diffusion coefficients D_{Am} calculated from eq 4 with the same $n = 1/3$ as found by Fukushima et al. (7) and the results obtained in this work, wherein the deviations are within 4%.

From such examinations, we may conclude that the solubility and the diffusion coefficient of CO₂ in various binary mixtures based on viscosity-composition curves are evaluated with a reasonable accuracy from eq 3 and 4 with $n = 1/3$, respectively.

Glossary

A_l	solubility of gas in liquid, mol/m ³
a	gas-liquid interfacial area, m ²
D	diffusion coefficient of gas in liquid, m ² /s
l	thickness of stagnant liquid film, m
n	constant of eq 4
N_A	absorption rate of gas into liquid, mol/(m ² s)
R	gas constant, J/(mol K)
T	temperature, K
t	gas-liquid contact time, s

V	volume of liquid-side cell, m ³
v	molar volume, m ³ /mol
x	mole fraction in liquid phase

Greek Letters

δ	solubility parameter, (kJ/m ³) ^{1/2}
ϵ	porosity of membrane
μ	viscosity, Pa s
ν	kinematic viscosity, m ² /s

Subscripts

A	diffusing component
B	B component in mixture (system of B-C)
C	C component in mixture (system of B-C)
i	component
m	mixture

Literature Cited

- O'Connell, J. P.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* **1964**, *3*, 347.
- Takeuchi, H.; Fujine, M.; Sato, T.; Onda, K. *J. Chem. Eng. Jpn.* **1975**, *8*, 252.
- Onda, K.; Takeuchi, H.; Fujine, M. *J. Chem. Eng. Jpn.* **1975**, *8*, 25.
- Ishikawa, T. "Kongoeki Nendo no Riron" ("Theories of Viscosity for Mixed Solvents"); Maruzen: Tokyo, 1968; Chapters 2 and 4.
- Davies, G. A.; Ponter, A. B.; Craine, K. *Can. J. Chem. Eng.* **1967**, *45*, 372.
- Dim, A.; Gardner, G. R.; Ponter, A. B.; Wood, T. J. *J. Chem. Eng. Jpn.* **1971**, *4*, 92.
- Fukushima, S.; Eto, Y.; Yokota, Y. Preprints of the 36th Annual Meeting of The Society of Chemical Engineers, Japan, Part 2, 1971, p 18.
- Hikita, H.; Nakanishi, K.; Kataoka, T. *Kagaku Kogaku* **1959**, *23*, 459.
- Onda, K.; Sada, E.; Kobayashi, T.; Ando, N.; Kito, S. *Kagaku Kogaku* **1970**, *34*, 603.
- Onda, K.; Takeuchi, H.; Kobayashi, T.; Takahashi, M.; Fujine, M. *Kagaku Kogaku* **1972**, *36*, 903.
- Tang, Y. P.; Himmelblau, D. M. *AIChE J.* **1965**, *11*, 54.
- Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik". 6. II Band, 2 Teil, Bandteil 6; Springer-Verlag: West Berlin, West Germany, 1962.
- Stephen, H.; Stephen, T. "Solubilities of Inorganic and Organic Compounds"; Pergamon Press: London, 1963; Vol. 1.
- Tokunaga, J.; Nitta, T.; Katayama, T. *Kagaku Kogaku* **1969**, *33*, 775.
- Tokunaga, J. *J. Chem. Eng. Data* **1975**, *20*, 41.
- Hildebrand, J. H.; Scott, R. L. "The Solubility of Nonelectrolytes", 3rd ed.; Reinhold: New York, 1950.
- Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley-Interscience: New York, 1970; Chapter 3.
- Hirata, M.; Ohe, S.; Nagahama, K. "Denshikaisanki ni yoru Kiekiheiko Data" ("Data of Gas-Liquid Equilibrium by Electronic Computer"), Part II; Kodansha Scientific: Tokyo, 1975.
- Kojima, K.; Tochigi, K.; Ochi, K. *Kagaku Kogaku* **1974**, *38*, 135.
- "Kagaku Benran" ("Handbook of Chemistry, Japan"); Maruzen: Tokyo, 1966.
- Shinoda, K. "Yoeki to Yokaido" ("Solutions and Solubilities"); Maruzen: Tokyo, 1966; Chapter 8.
- Takahashi, M.; Takeuchi, H.; Onda, K. *Kagaku Kogaku Ronbunshu* **1975**, *1*, 634.

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Excess Volumes of Binary Mixtures of *o*-Xylene + *n*-Alkanes

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Excess volumes of the binary mixtures *o*-xylene + *n*-hexane, + *n*-octane, + *n*-decane, + *n*-dodecane, + *n*-tetradecane, and + *n*-hexadecane have been measured at 298.15 K as a function of composition. Measurements were made in a semicontinuous dilution dilatometer.

Introduction

Excess volume measurements of hydrocarbon mixtures have been widely used to check liquid-state theories. Binary mixtures of xylene + *n*-alkanes have been chosen to extend our investigations in order to study the influence of methyl groups and

Table I. Experimental Excess Volumes V^E at 298.15 K

x	$V^E/$ ($\text{cm}^3 \text{mol}^{-1}$)	x	$V^E/$ ($\text{cm}^3 \text{mol}^{-1}$)	x	$V^E/$ ($\text{cm}^3 \text{mol}^{-1}$)
<i>o</i> -Xylene + <i>n</i> -Hexane					
0.0958	-0.1089	0.4427	-0.3261	0.7487	-0.2481
0.2259	-0.2258	0.4850	-0.3265	0.7920	-0.2164
0.3451	-0.2968	0.5069	-0.3275	0.9020	-0.1134
0.3862	-0.3124	0.6079	-0.3098	0.9619	-0.0459
0.3965	-0.3161	0.6957	-0.2793		
<i>o</i> -Xylene + <i>n</i> -Octane					
0.0408	0.0036	0.3217	0.0008	0.6049	-0.0190
0.1047	0.0056	0.4168	-0.0065	0.6094	-0.0186
0.1524	0.0056	0.4462	-0.0095	0.6733	-0.0238
0.2219	0.0043	0.5053	-0.0142	0.7579	-0.0216
0.2656	0.0033	0.5492	0.0171	0.9477	-0.0078
<i>o</i> -Xylene + <i>n</i> -Decane					
0.0737	0.0381	0.5798	0.1433	0.7989	0.0963
0.1852	0.0840	0.6105	0.1398	0.8690	0.0679
0.2039	0.0921	0.6205	0.1377	0.9414	0.0320
0.4377	0.1427	0.6705	0.1291	0.9780	0.0108
0.4573	0.1432	0.7143	0.1233		
0.5228	0.1458	0.7784	0.1055		
<i>o</i> -Xylene + <i>n</i> -Dodecane					
0.1082	0.0734	0.5455	0.2317	0.7421	0.2005
0.2074	0.1337	0.5913	0.2294	0.8017	0.1709
0.2826	0.1698	0.6019	0.2309	0.8130	0.1623
0.4128	0.2140	0.6316	0.2240	0.8787	0.1200
0.4354	0.2202	0.6418	0.2242	0.9433	0.0583
0.4925	0.2291	0.6435	0.2249	0.9460	0.0562
0.5005	0.2289	0.6830	0.2166	0.9796	0.0255
<i>o</i> -Xylene + <i>n</i> -Tetradecane					
0.0980	0.0800	0.5831	0.2865	0.7140	0.2618
0.2624	0.1899	0.6261	0.2836	0.7564	0.2429
0.3890	0.2489	0.6207	0.2824	0.7719	0.2378
0.4916	0.2752	0.6285	0.2823	0.8583	0.1751
0.5301	0.2814	0.6613	0.2770	0.9096	0.1234
0.5657	0.2833	0.6780	0.2733	0.9602	0.0607
0.5751	0.2845	0.6929	0.2710	0.9848	0.0242
<i>o</i> -Xylene + <i>n</i> -Hexadecane					
0.1098	0.0922	0.6144	0.3202	0.7967	0.2488
0.2848	0.2176	0.6672	0.3120	0.8524	0.2066
0.4158	0.2852	0.7038	0.3008	0.9063	0.1447
0.5710	0.3212	0.7474	0.2818	0.9591	0.0664

their relative position in the aromatic ring on the excess volume.

In this paper we report the results for mixtures of *o*-xylene + *n*-alkanes. We have found no data for these systems in the consulted literature (1-3). The results for binary mixtures of *p*-xylene + *n*-alkanes and benzene + *n*-alkanes have been previously published (4, 5). The excess volumes for binary mixtures of *m*-xylene + *n*-alkanes will be reported in a future paper.

Experimental Section

Excess Volume Measurements. The excess volume was measured as a function of composition by a dilatometric method which is a modification of the one given in ref 6 and is described in detail elsewhere (4). Two overlapping dilution runs were required to cover the whole mole fraction range for each system. The accuracy of any individual measurement of excess volume was better than $0.001 \text{ cm}^3 \text{ mol}^{-1}$.

Table II. Parameters in Smoothing Eq 1, Their Respective Standard Deviations, and Standard Deviations for Excess Volumes, $\sigma(V^E)$

systems	A_0	$\sigma(A_0)$	A_1	$\sigma(A_1)$	A_2	$\sigma(A_2)$	A_3	$\sigma(A_3)$	$\sigma(V^E)/$ ($\text{cm}^3 \text{mol}^{-1}$)
<i>o</i> -xylene + <i>n</i> -hexane	-1.320	0.004	-0.012	0.006	0.078	0.011			0.0021
<i>o</i> -xylene + <i>n</i> -octane	-0.053	0.002	-0.135	0.004	0.018	0.007			0.0009
<i>o</i> -xylene + <i>n</i> -decane	0.582	0.006	0.074	0.020	-0.025	0.017	-0.109	0.034	0.0018
<i>o</i> -xylene + <i>n</i> -dodecane	0.914	0.009	0.206	0.024	0.074	0.035			0.0018
<i>o</i> -xylene + <i>n</i> -tetradecane	1.112	0.003	0.332	0.009	0.139	0.008	0.058	0.001	0.0009
<i>o</i> -xylene + <i>n</i> -hexadecane	1.248	0.028	0.455	0.041	0.079	0.068			0.0018

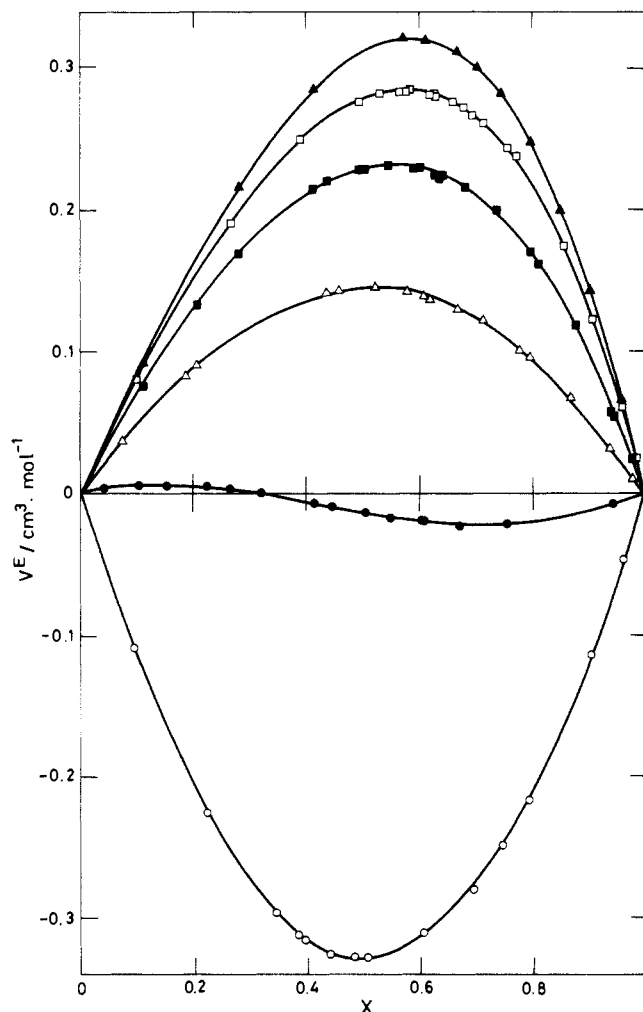


Figure 1. Excess volumes V^E against the mole fraction, x , of *o*-xylene: (O) *o*-xylene + *n*-hexane; (●) *o*-xylene + *n*-octane; (Δ) *o*-xylene + *n*-decane; (■) *o*-xylene + *n*-dodecane; (□) *o*-xylene + *n*-tetradecane; (▲) *o*-xylene + *n*-hexadecane.

Materials. The alkanes are the same as the ones used in previous work (7). *o*-Xylene (Carlo Erba RPE) has been treated with sodium and used with no further purification. The purity of the *o*-xylene was tested by comparing the experimental density and refractive index with literature data; gas-chromatography analysis was also used as a criterion of purity.

The experimental density at 298.15 K was found to be $0.87505 \text{ g cm}^{-3}$ compared with the literature value of $0.87583 \text{ g cm}^{-3}$ (8). The experimental refraction index, n_D (303.15 K), was 1.49960. The literature value was 1.50025 (8).

Results

All of the systems were measured at 298.15 K. The experimental excess volumes are given in Table I and plotted in Figure 1.

The experimental results were fitted to an equation of the type

$$V^E/[x(1-x)] = \sum A_i(2x-1)^i \quad (1)$$

where x is the mole fraction of *o*-xylene for all of the systems. The solid lines of Figure 1 are those calculated from the smoothing equation. The coefficients of eq 1, their respective standard deviations, and the standard deviations for the excess volumes are given in Table II.

The results for these systems can be compared with those obtained for benzene + *n*-alkanes (5) and *p*-xylene + *n*-alkanes (4). Both *o*-xylene and *p*-xylene + *n*-alkanes systems show a very similar behavior. Excess volumes are slightly smaller for those systems where *p*-xylene is one of the compounds. The most remarkable difference is that the excess volume for *o*-xylene + *n*-octane changes sign (from positive to negative) as the mole fraction of *o*-xylene increases, while *p*-xylene + *n*-octane always shows a positive excess volume.

The excess volumes for benzene + *n*-alkanes are always positive and are larger than those found for xylene + *n*-alkanes. These systems show a more ideal behavior which is probably due to the methyl groups in the aromatic ring.

Literature Cited

- (1) Timmermans, J. "Physico-Chemical Constants of Binary Systems"; Interscience: New York, 1959; Vol. 1.
- (2) Battino R. *Chem. Rev.* 1971, 71, 5.
- (3) Handa, Y. P.; Benson G. C. *Fluid Phase Equilib.* 1979, 3, 185.
- (4) Cáceres Alonso, M.; Nuñez Delgado, J. *J. Chem. Thermodyn.* 1981, 13, 1133.
- (5) Diaz Peña, M.; Nuñez Delgado, J. *An. Quim.* 1974, 70, 678.
- (6) Diaz Peña, M.; Nuñez Delgado, J. *An. Quim.* 1977, 73, 24.
- (7) Diaz Peña, M.; Nuñez Delgado, J. *J. Chem. Thermodyn.* 1975, 7, 201.
- (8) Dreisbach, R. R. "Advances in Chemistry Series"; American Chemical Society: Washington, DC, 1955; No. 15, p 14.

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Excess Enthalpies of Binary Systems of Cyclic Ether + Cyclohexene

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The molar excess enthalpy H^E has been measured as a function of mole fraction x at atmospheric pressure and 298.15 K for the binary liquid systems cyclohexene (C_6H_{10}) + oxolane (tetrahydrofuran, C_4H_8O), + oxane (tetrahydropyran, $C_5H_{10}O$), + 1,3-dioxolane ($1,3-C_3H_4O_2$), + 1,4-dioxane ($1,4-C_4H_8O_2$), and + cyclohexane (C_6H_{12}), by using a flow calorimeter of the Picker design. The mixtures with cyclic diethers exhibit relatively large positive excess enthalpies: for 1,3- $C_3H_4O_2$ + C_6H_{10} , $H^E(x=0.5) = 1155.5 \text{ J mol}^{-1}$; and for 1,4- $C_4H_8O_2$ + C_6H_{10} , $H^E(x=0.5) = 909.7 \text{ J mol}^{-1}$. The excess enthalpy for C_4H_8O + C_6H_{10} is considerably smaller, i.e., $H^E(x=0.5) = 285.5 \text{ J mol}^{-1}$, and $C_5H_{10}O$ + C_6H_{10} shows S-shaped dependence of H^E on x , with the very small negative section being located at small mole fractions of the cyclic ether ($x < 0.0899$). For C_6H_{12} + C_6H_{10} the excess enthalpy is rather symmetric, with $H^E(x=0.5) = 97.3 \text{ J mol}^{-1}$.

Introduction

Excess enthalpies of binary liquid mixtures composed of either five- or six-membered cyclic ethers and various second components (ranging from *n*-alkanes to alkanolic acids) were reported in ref 1-5. As a sequel, we present here measurements of the molar excess enthalpy H^E at 298.15 K of the binary systems cyclohexene (C_6H_{10}) + oxolane (tetrahydrofuran, C_4H_8O), + oxane (tetrahydropyran, $C_5H_{10}O$), + 1,3-dioxolane ($1,3-C_3H_4O_2$), + 1,4-dioxane ($1,4-C_4H_8O_2$), and + cyclohexane (C_6H_{12}). These measurements will be used later to assess, in terms of group-contribution theory (δ), the influ-

Table I. Densities (ρ) of Pure Component Liquids at 298.15 K

compd	$\rho/(\text{kg m}^{-3})$	
	exptl	lit.
cyclohexene	806.0	806.09 (9), 806.3, ^a 805.66 (11), 805.9 (12), 805.70 (13)
cyclohexane	773.9	773.89 (14)
oxane	879.1	879.22 ^b
oxolane	881.9	881.97 (16)
1,4-dioxane	1028.2	1028.21 (17), 1027.97 (18)
1,3-dioxolane	1059.1	1053.8 ^c

^a Interpolated value from ref 10. ^b Interpolated value from ref 15. ^c Extrapolated value from ref 19.

Table II. Comparison of Experimental Molar Excess Enthalpies H^E at 298.15 K of the Test System Benzene (x) + Cyclohexane ($1-x$) with the Results of Marsh (20)

x	$H^E/(\text{J mol}^{-1})$		δ^a
	exptl	Marsh (20)	
0.2118	519.3	523.8	-0.9
0.3064	667.2	669.7	-0.4
0.4015	756.2	761.8	-0.7
0.4920	793.7	798.5	-0.6
0.5768	779.9	787.2	-0.9
0.6581	729.3	733.8	-0.6
0.7400	638.3	636.2	+0.3
0.9334	214.6	214.7	0.0

^a Percentage deviation $\delta = 100(H^E_{\text{exptl}} - H^E_{\text{Marsh}})/H^E_{\text{Marsh}}$.

ence of various structural parameters (ring size, proximity of oxygen in diethers, $n-\pi$ interaction, etc.) on the thermodynamic behavior of such mixtures.

Experimental Section

Materials. Source and treatment of the cycloethers have been given previously (1). Cyclohexene (from Fluka, puriss.,

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