V_L	molal volume of liquid, ft^3 lb-mol^{-1}
V_V	molal volume of vapor, ft^3 lb-mol^{-1}
x	mole fraction of component in liquid phase
x_2	mole fraction of solute in liquid phase
y	mole fraction of component in vapor phase
ρ	molal density, g-mol mL^{-1}

Literature Cited

(1) Benedict, M., Webb, G. B., Rubin, L. C., *J. Chem. Phys.*, **8**, 334 (1940).
(2) Besserer, G. J., Robinson, D. B., *Can. J. Chem. Eng.*, **49** (5), 651 (1971).
(3) Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data*, **18**, 298 (1973).
(4) Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data*, **20** 157 (1975).
(5) Bishnoi, P. R., Miranda, R. D., Robinson, D. B., *Hydrocarbon Process.*, **53** (11), 197 (1974).
(6) Christiansen, L. J., Fredenslund, A., *AIChE J.*, **21**, 49 (1975).
(7) Keilich, S., *Physica (Utrecht)*, **28**, 1116 (1962).
(8) Kurata, F., Swift, G. W., NGPA Research Report RR-5, Dec 1971.
(9) Lorentz, H. *Justus Liebigs Ann. Chem.*, **9**, 641 (1880).
(10) Lorenz, L., *Justus Liebigs Ann. Chem.*, **11**, 70 (1880).
(11) Miranda, R. D., Robinson, D. B., Kalra, H., *J. Chem. Eng. Data*, **21**, 62 (1976).
(12) Smyth, C. P., Engel, E. W., Wilson, Jr., E. B., *J. Am. Chem. Soc.*, **51**, 1736 (1929).

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Volume Changes on Mixing Normal Alkanes with Branched Alkanes

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Excess volumes at 25 °C are reported for the systems *n*-pentane + 2,6-dimethylheptane, *n*-hexane + 2,5-dimethylhexane, *n*-heptane + 2,4-dimethylpentane and *n*-octane + 2,3-dimethylbutane. The results are compared with the predictions of a generalized principle of congruence.

The principle of congruence is a very useful tool for predicting the properties of hydrocarbon mixtures. As originally formulated by Brønsted and Koefoed (*1*), the principle asserts that at a given temperature the properties of mixtures of *n*-alkanes depend only on the average chain length $\bar{n}$

$$\bar{n} = \sum_i x_i n_i \qquad (1)$$

where x_i is the mole fraction of component i and n_i is its chain length. The principle has been extended with some success to other homologous series (*2*) and has been found applicable to gaseous mixtures as well (*3, 7*).

Theoretical justification for the principle of congruence was provided by Longuet-Higgins (*4*). His model for the interactions between long-chain molecules of similar type leads to a generalization of the congruence principle: "if two mixtures, each containing chain molecules of the type $A(X)_nB$, are such that the molecules of the two mixtures can be divided into identical sets of fragments by cutting the chains in suitable places, then these mixtures will have identical equations of state and identical solvent properties."

The systems *n*-pentane + 2,6-dimethylheptane, *n*-hexane + 2,5-dimethylhexane, *n*-heptane + 2,4-dimethylpentane, and *n*-octane + 2,3-dimethylbutane might be expected to satisfy the

Table I. Excess Volumes, V_m^E, at 25 °C

x	V_m^E/cm^3 mol^{-1}	x	V_m^E/cm^3 mol^{-1}	x	V_m^E/cm^3 mol^{-1}	x	V_m^E/cm^3 mol^{-1}
	n-Pentane + 2,6-Dimethylheptane				*n*-Heptane + 2,4-Dimethylpentane		
0.0263	−0.037	0.4805	−0.260	0.0317	−0.0114	0.4623	−0.0347
0.0625	−0.080	0.4869	−0.258	0.0716	−0.0161	0.5043	−0.0347
0.1081	−0.127	0.5230	−0.252	0.1671	−0.0240	0.5205	−0.0340
0.1614	−0.172	0.5445	−0.248	0.2290	−0.0280	0.5488	−0.0348
0.2169	−0.207	0.5568	−0.245	0.2941	−0.0314	0.6004	−0.0338
0.2769	−0.234	0.6249	−0.221	0.3509	−0.0333	0.6590	−0.0315
0.3306	−0.251	0.6933	−0.192	0.3533	−0.0315	0.7326	−0.0274
0.3637	−0.258	0.7654	−0.156	0.4011	−0.0334	0.8132	−0.0214
0.3804	−0.258	0.8333	−0.118	0.4114	−0.0344	0.9062	−0.0128
0.4188	−0.263	0.8982	−0.075	0.4465	−0.0341		
0.4336	−0.261	0.9611	−0.029				
	n-Hexane + 2,5-Dimethylhexane						
0.0446	−0.0030	0.5248	−0.0232		*n*-Octane + 2,3-Dimethylbutane		
0.1010	−0.0072	0.5434	−0.0222	0.0496	−0.021	0.5352	−0.129
0.1750	−0.0126	0.5878	−0.0217	0.0944	−0.039	0.5434	−0.124
0.2419	−0.0165	0.5925	−0.0221	0.2083	−0.077	0.5861	−0.129
0.3252	−0.0203	0.6305	−0.0209	0.2534	−0.089	0.6012	−0.122
0.3925	−0.0221	0.6704	−0.0200	0.2992	−0.100	0.6749	−0.115
0.4228	−0.0224	0.7299	−0.0176	0.3691	−0.114	0.7567	−0.100
0.4519	−0.0225	0.8041	−0.0144	0.4190	−0.115	0.8537	−0.070
0.4656	−0.0230	0.8842	−0.0078	0.4337	−0.123	0.9234	−0.046
0.4811	−0.0228	0.9512	−0.0029	0.4893	−0.122	0.9593	−0.023
0.5128	−0.0228			0.4933	−0.128		

Table II. Parameters in Smoothing Equation 2, Their Respective Standard Deviations, and Standard Deviations for Excess Volumes, $\sigma(V_m^E)$

System	v_0	$\sigma(v_0)$	v_1	$\sigma(v_1)$	v_2	$\sigma(v_2)$	$\sigma(V_m^E)$/cm^3 mol^{-1}
n-Pentane + 2,6-dimethylheptane	−1.022	0.001	−0.315	0.004	−0.067	0.008	0.0011
n-Hexane + 2,5-dimethylhexane	−0.092	0.001	−0.002	0.002	0.015	0.003	0.0004
n-Heptane + 2,4-dimethylpentane	−0.136	0.002	−0.018	0.007	−0.063	0.015	0.0017
n-Octane + 2,3-dimethylbutane	−0.501	0.003	0.076	0.009	−0.034	0.020	0.0024

general principle of congruence. Equimolar mixtures can conceptually be divided into identical sets of fragments, sets which could also be obtained from pure 2-methylhexane. The present study was undertaken to test the applicability of congruence to these systems.

Experimental Section

Volume Change Measurements. The measurements were made in a continuous dilution dilatometer described elsewhere (*5*). The temperature was measured with a 25 Ω platinum resistance thermometer calibrated by the U.S. National Bureau of Standards. In order to cover the entire mole fraction range, two overlapping dilution runs were made for each system. Densities of the pure components were taken from the API tables (*6*).

Materials. *n*-Pentane, *n*-hexane, 2,3-dimethylbutane, *n*-heptane, and *n*-octane were obtained from Phillips Petroleum Co. The reported purity of these chemicals was 99.93, 99.99, 99.89, 99.98, and 99.92 mol %, respectively, and they were used without further purification. 2,4-Dimethylpentane, 2,5-dimethylhexane, and 2,6-dimethylheptane with reported purities of 99.7, 99, and 99 mol %, respectively, were obtained from Chemical Samples Co. These chemicals were further purified by successive washings with H_2SO_4, Na_2CO_3, and distilled water. All materials were dried over freshly activated molecular sieve (Union Carbide, type 4A), degassed by vacuum sublimation, and stored in mercury-sealed bulbs.

Results and Discussion

The systems *n*-pentane + 2,6-dimethylheptane, *n*-hexane + 2,5-dimethylhexane, *n*-heptane + 2,4-dimethylpentane, and *n*-octane + 2,3-dimethylbutane were investigated at 25 °C. The experimentally determined excess volumes are given in Table I, and a graphical representation is given in Figures 1 and 2.

The excess volumes were fitted to a smoothing equation of the type

$$V_m^E/\text{cm}^3\ \text{mol}^{-1} = x(1-x)[v_0 + v_1(1-2x) + v_2(1-2x)^2] \quad (2)$$

where x refers to the mole fraction of the second-named component. Values of the parameters v_0, v_1, and v_2, their respective standard deviations, and the standard deviations for the excess volumes are given in Table II.

According to the generalized principle of congruence, at $x = 0.5$ each of the four systems should be congruent with 2-methylhexane. Thus at $x = 0.5$, the excess volume of each of the four systems should be equal to the difference between the molar volume of 2-methylhexane and one-half the sum of the molar volumes of the pure components. Table III shows a comparison of the experimentally determined and the predicted excess volumes for equimolar mixtures at 25 °C. Molar volumes of the hydrocarbons have been taken from the API tables (*6*).

The uncertainties in the tabulated densities of the pure components are specified as lying in the range 0.002–0.0002 g cm^{-3}. If one assumes the uncertainties to be minimal, the calculated excess volumes are known to about 0.04 cm^3 mol^{-1}. Although the generalized principle of congruence is seen to reproduce the trends in the first three systems, it does not predict these rather small volume changes very accurately and fails even to predict the sign of V_m^E for *n*-octane + 2,3-dimethylbutane.

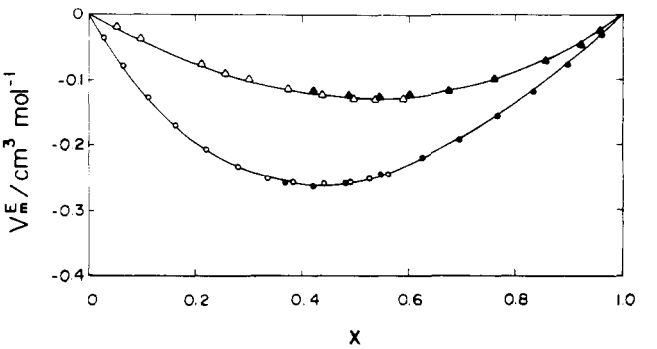

Figure 1. Excess volumes at 25 °C. Open and closed symbols represent two dilution runs. Upper curve is for *n*-octane + 2,3-dimethylbutane and the lower curve is for *n*-pentane + 2,6-dimethylheptane.

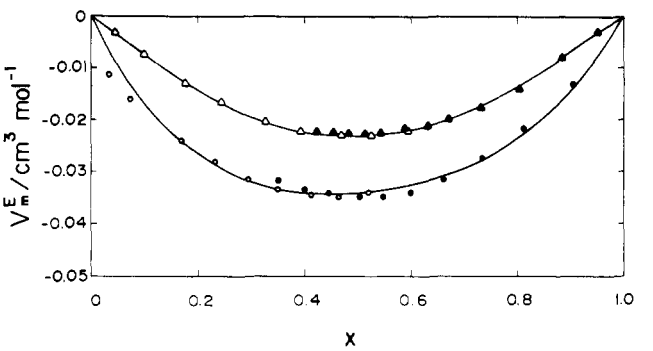

Figure 2. Excess volumes at 25 °C. Open and closed symbols represent two dilution runs. Upper curve is for *n*-hexane + 2,5-dimethylhexane and the lower curve is for *n*-heptane + 2,4-dimethylpentane.

Table III. Excess Volumes at $x = 0.5$, 25 °C

Equimolar mixture of	V_m^E(exptl)/ cm^3 mol^{-1}	V_m^E(calcd)/ cm^3 mol^{-1}
n-Pentane + 2,6-dimethylheptane	−0.256	−0.447
n-Hexane + 2,5-dimethylhexane	−0.023	−0.073
n-Heptane + 2,4-dimethylpentane	−0.034	−0.115
n-Octane + 2,3-dimethylbutane	−0.125	1.233

One would hardly expect 2,3-dimethylbutane, where the isopropyl groups are adjacent, to follow the principle of congruence. Moreover, in retrospect, it is not surprising that there are substantial discrepancies in the other systems since the molar volumes of the pure branched hydrocarbons do not vary smoothly with chain length (*6*).

Literature Cited

(1) Brønsted, J. N., Koefoed, J., *K. Dan. Vidensk. Selsk., Mat-Fys. Medd.*, **22** (17), 32 (1946).
(2) Brown, I., *Annu. Rev. Phys. Chem.*, **16**, 147 (1965).
(3) Dantzler, E. M., Knobler, C. M., Windsor, M. L., *J. Phys. Chem.*, **72**, 676 (1968).
(4) Longuet-Higgins, H. C., *Discuss. Faraday Soc.*, **15**, 73 (1953).
(5) Reeder, J., Knobler, C. M., Scott, R. L., *J. Chem. Thermodyn.*, **7**, 345 (1975).
(6) Rossini, F. D., Ed., *Am. Pet. Inst.*, Project 44 Tables (1953).
(7) Williamson, A. G., Pandya, M. V., *Aust. J. Chem.*, **24**, 465 (1971).

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