ρ	density, g cm^{-3}
τ	period of oscillation
σ	standard deviation
δ	deviation between calculated and experimental values, cm^3 mol^{-1}

Registry No. Methanol, 67-56-1; heptane, 142-82-5; ethyl acetate, 141-78-6; butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2.

Literature Cited

(1) Eng, R.; Sandler, S. I. *J. Chem. Eng. Data* **1984**, *29*, 156.
(2) Shealy, G. S.; Sandler, S. I. *J. Chem. Thermodyn.*, in press.
(3) Wilhelm, E.; Grolier, J. P. E.; Karbalai Ghassemi, M. H. *Monatsh. Chem.* **1978**, *109*, 369.
(4) Grolier, J. P. E.; Karbalai Ghassemi, M. H.; Inglese, A. *Int. Data Ser., Ser. B* **1977**, Guideline 2c.

(5) Goates, J. R.; Otts, J. B.; Moellmer, J. F. *J. Chem. Thermodyn.* **1977**, *9*, 249.
(6) Takenaka, M.; Tanaka, R.; Murakami, S. *J. Chem. Thermodyn.* **1980**, *12*, 849.
(7) Riddick, J. A.; Bunger, E. B. "Organic Solvents. Physical Properties and Methods of Purification"; Wiley-Interscience: New York, 1970.
(8) Davies, O. L.; Goldsmith, P. L. "Statistical Methods in Research and Production"; Hafner Publishing Co.: New York, 1972.
(9) Mikhail, S. Z.; Kimel, W. R. *J. Chem. Eng. Data* **1961**, *6*, 533.
(10) Grolier, J. P. E.; Ballet, D.; Viallard, A. *J. Chem. Thermodyn.* **1974**, *6*, 895.

Excess Enthalpies of Binary Mixtures of 2,4-Dimethylpentane with n-Hexane, n-Heptane, n-Octane, and n-Dodecane[†]

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Calorimetric measurements of excess enthalpies are reported for binary mixtures of 2,4-dimethylpentane with n-hexane, n-heptane, n-octane, and n-dodecane at 298.15 K. The results for the mixtures containing n-hexane and n-octane are much lower than previous estimates of excess enthalpies obtained from vapor–liquid equilibria.

The effect of chain branching on the excess thermodynamic properties of binary mixtures has been investigated previously in our laboratory by measuring excess enthalpies for mixtures of n-heptane (1), n-octane (2), and n-dodecane (3) with each of the five hexane isomers. The present paper reports the results of similar measurements for mixtures of a branched isomer of n-heptane, 2,4-dimethylpentane (2,4-DMP), with the n-alkanes: n-hexane, n-heptane, n-octane, and n-dodecane.

Experimental Section

Excess molar enthalpies, H_m^E, were determined at 298.15 K in a modified LKB flow microcalorimeter. Details of the equipment and its operation have been described previously (1, 4). For most of the measurements the error in the determination of H_m^E is estimated to be less than 0.5%. However, it may be somewhat higher for small H_m^E (<10 J mol^{-1}).

Sources of the component liquids and purities specified by the manufacturers are summarized in Table I. In all cases the liquids were used without further purification. Densities, measured at 298.15 K in an Anton Paar densimeter, are also listed in Table I along with values from the literature (5) for comparison.

Results and Discussion

The experimental values of H_m^E, measured for the four 2,4-DMP–n-alkane systems at 298.15 K, are given in Table II. In

Table I. Sources, Purities, and Densities, $\rho(T = 298.15 \text{ K})$, of the Component Liquids

		$\rho/(\text{kg m}^{-3})$	
liquid	source and purity	obsd	lit. (5)
2,4-dimethyl-pentane	Phillips Petroleum Co., Research Grade, 99.72 mol %	668.44	668.32
n-hexane	Phillips Petroleum Co., Research Grade, 99.95 mol %	654.92	654.84
n-heptane	Phillips Petroleum Co., Pure Grade, >99 mol %	679.67	679.46
n-octane	Aldrich Chemical Co., Gold Label, >99 mol %	698.61	698.62
n-dodecane	Phillips Petroleum Co., Pure Grade, >99 mol %	745.23	745.18

all cases, x is the mole fraction of 2,4-DMP.

The parameters of the smoothing equation

$$H_m^E/(\text{J mol}^{-1}) = x(1 - x)[1 - k(1 - 2x)]^{-1} \sum_{j=1}^{m} h_j(1 - 2x)^{j-1}$$

(1)

were fitted to each set of results by the method of least squares with each point assigned unit weight. The skewing factor k was set equal to zero except for the mixture with n-dodecane. In the latter instance fewer coefficients h_j were needed to fit the results adequately when k was also treated as an adjustable parameter. The values of h_j and k, obtained from the least-squares analyses, are listed in Table III, along with the standard deviations, s, of the representations.

The experimental results and their representations by eq 1 are plotted in Figure 1. For each mixture, H_m^E is positive throughout the mole fraction range and is appreciably greater than the H_m^E for the corresponding n-heptane–n-alkane mixture (1, 6, 7).

We are not aware of any comparable previous calorimetric studies of the present mixtures. Values of H_m^E for 2,4-DMP with n-hexane at 293.15 K and with n-octane at 303.15 K have been estimated by Davison and co-workers (8, 9) from measurements of vapor–liquid equilibria over the range 283.15–313.15 K. Allowing for the differences of temperature, these values of H_m^E are very much larger than our calorimetric results and it appears that the discrepancies must be attributed

Table II. Experimental Results for the Excess Molar Enthalpy, $H_m{}^E$, of 2,4-Dimethylpentane-n-Alkane Mixtures at 298.15 K and Mole Fraction, x, of 2,4-Dimethylpentane

x	$H_m{}^E/$ (J mol^{-1})	x	$H_m{}^E/$ (J mol^{-1})	x	$H_m{}^E/$ (J mol^{-1})	x	$H_m{}^E/$ (J mol^{-1})
			2,4-DMP–n-Hexane				
0.0502	1.67	0.2996	6.54	0.5503	7.48	0.7999	4.76
0.0998	2.84	0.3505	7.09	0.6009	7.27	0.8498	3.70
0.1500	4.06	0.3988	7.39	0.6499	6.74	0.8997	2.67
0.1992	5.11	0.4505	7.61	0.6998	6.17	0.9499	1.30
0.2501	5.88	0.5006	7.66	0.7499	5.50		
			2,4-DMP–n-Heptane				
0.1001	8.49	0.3997	21.98	0.6001	22.16	0.7998	14.81
0.1997	14.79	0.4996	22.99	0.6999	19.23	0.9005	8.14
0.2999	19.18						
			2,4-DMP–n-Octane				
0.1041	12.90	0.2498	25.78	0.5004	34.61	0.7999	22.37
0.1997	21.85	0.3178	29.80	0.6003	33.23	0.8499	18.22
0.2074	22.80	0.4002	33.04	0.6995	29.40	0.8999	12.89
			2,4-DMP–n-Dodecane				
0.0501	17.83	0.3996	107.69	0.6050	109.67	0.8002	14.91
0.1002	36.93	0.4324	110.52	0.6997	97.27	0.8999	42.80
0.2002	69.76	0.4998	113.30	0.7529	86.65	0.9500	22.81
0.3004	93.25	0.6000	109.96				

Table III. Coefficients, h_j, Skewing Factor, k, and Standard Deviation, s, for Representations of $H_m{}^E$ at 298.15 K for 2,4-Dimethylpentane-n-Alkane Mixtures by Eq 1

n-alkane	h_1	h_2	h_3	h_4	k	s
n-hexane	30.49	2.06				0.05
n-heptane	91.94					0.12
n-octane	138.06	-2.69	3.62			0.12
n-dodecane	453.50	-450.98	22.03	-13.85	0.9465	0.10

to the inaccuracy associated with the derivation of the excess enthalpy from the temperature variation of the excess Gibbs free energy.

Several ways of correlating the results for the four systems were investigated. It was found that a semiquantitative interpretation of the enthalpies was possible by using the generalized quasi-chemical theory in terms of group surface interactions, as formulated by Kehiaian et al. (10). The component molecules were assumed to contain three types of surface—a, b, and c—corresponding to CH_3, CH_2, and CH groups, respectively. In the zero approximation, the formula for $H_m{}^E$ becomes

$$H_m{}^E = -x(1-x)q_1q_2[xq_1 + (1-x)q_2]^{-1}[(\alpha_{a,1} - \alpha_{a,2}) \times$$
$$(\alpha_{b,1} - \alpha_{b,2})h_{ab} + (\alpha_{a,1} - \alpha_{a,2})(\alpha_{c,1} - \alpha_{c,2})h_{ac} + (\alpha_{b,1} - \alpha_{b,2})(\alpha_{c,1} - \alpha_{c,2})h_{bc}] \quad (2)$$

where q_i is the ratio between the molecular surface area of component i (1 = 2,4-DMP, 2 = n-alkane) and that of a selected reference molecule, $\alpha_{s,i}$ is the surface fraction of type s surface in component i, and h_{st} is the molar interchange enthalpy for unit relative molecular surface area of contact between surfaces of types s and t. Molecular and group surface areas were obtained from the work of Bondi (11). Values of q_i (stated relative to the molecular surface area of CH_4 as a reference) and of $\alpha_{s,i}$ are summarized in Table IV. The interchange parameters h_{st} were adjusted to minimize the sum of squares of the deviations between calculated and smoothed experimental values of $H_m{}^E$ at x = 0.25, 0.50, and 0.75 for the four systems. This analysis led to h_{st} = 1.465, 72.652, and 53.779 kJ mol^{-1} for unit relative molecular surface areas of contact of the types ab, ac and bc, respectively. The broken curves in Figure 1 were calculated from eq 2 by using these values. The agreement with the experimental curves is reasonable in view of the simple form of the theory. It appears that with increasing chain length of the n-alkane, the calculated curves become more skewed toward x = 1 than the curves observed experimentally. The same parameters were also
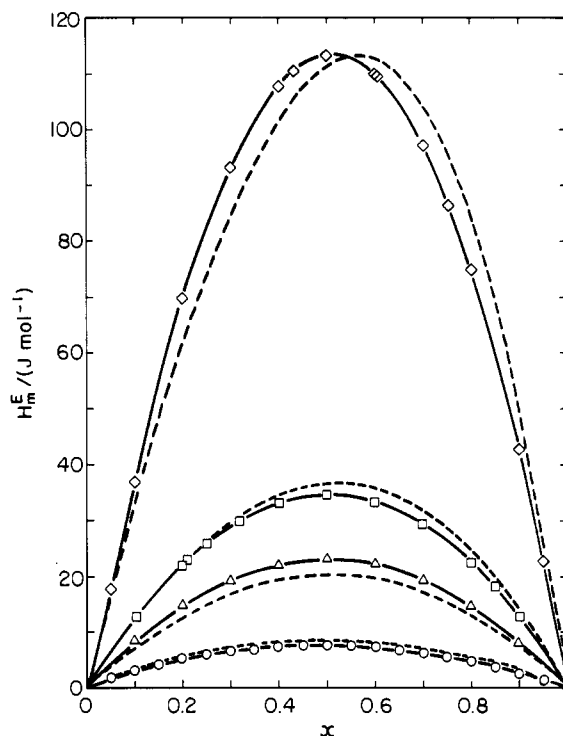
Figure 1. Excess molar enthalpy, $H_m{}^E$, of 2,4-dimethylpentane-n-alkane mixtures at 298.15 K and mole fraction, x, of 2,4-dimethylpentane: (O) n-hexane; (△) n-heptane; (□) n-octane; (◇) n-dodecane. Curves: (—) calculated from eq 1 with h_j and k from Table III; (– – –) calculated from eq 2 with q_i and $\alpha_{s,i}$ from Table IV and h_{st} stated in text.

Table IV. Relative Molecular Surface Area, q_i,[a] and Group Surface Fractions, $\alpha_{s,i}$,[b] for the Component Molecules

component i	q_i	$\alpha_{a,i}$	$\alpha_{b,i}$	$\alpha_{c,i}$
2,4-DMP	3.5862	0.8154	0.1298	0.0548
n-hexane	3.3241	0.4398	0.5602	0.0
n-heptane	3.7897	0.3858	0.6142	0.0
n-octane	4.2552	0.3436	0.6564	0.0
n-dodecane	6.1172	0.2390	0.7610	0.0

[a] Stated relative to 2.90 × 10^5 m^2 mol^{-1} for CH_4. [b] a = CH_3, b = CH_2, c = CH.

used to estimate $H_m{}^E$ for binary n-alkane mixtures. Reasonable estimates were obtained for several mixtures with differences

of chain length <5 but H_m^E was overestimated significantly for mixtures involving larger differences. Thus, some discretion must be exercised if the parameters obtained above are used for mixtures other than those studied in the present work.

Acknowledgment

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Glossary

H_m^E	excess molar enthalpy, J mol^{-1}
h_j	coefficients in eq 1
h_{st}	molar interchange enthalpy per unit relative molecular surface area for contact between surfaces of types s and t
k	skewing factor in eq 1
q_i	relative molecular surface area of component i
x	mole fraction of 2,4-dimethylpentane

Greek Letters

$\alpha_{s,i}$	surface fraction of type s surface in component i

Literature Cited

(1) Kimura, F.; Benson, G. C.; Halpin, C. J. *Fluid Phase Equilib*. **1983**, *11*, 245.
(2) Hamam, S. E. M.; Kumaran, M. K.; Benson, G. C. *Fluid Phase Equilib*. **1984**, *18*, 147.
(3) Hamam, S. E. M.; Kumaran, M. K.; Benson, G. C. *J. Chem. Thermodyn*. **1984**, *16*, 537.
(4) Tanaka, R.; D'Arcy, P. J.; Benson, G. C. *Thermochim. Acta* **1975**, *11*, 163.
(5) "Selected Values of Properties of Hydrocarbons and Related Compounds, Thermodynamics Research Center Hydrocarbon Data Project"; Thermodynamics Research Center, Texas A & M University: College Station, TX. See Tables 23-2-(1.101)-a and 23-2-(1.202)-a.
(6) Burchfield, T. E.; Bertrand, G. L. *J. Solution Chem*. **1975**, *4*, 205.
(7) Kumaran, M. K.; Benson, G. C., to be submitted for publication.
(8) Ho, C. L.; Davison, R. R. *J. Chem. Eng. Data* **1979**, *24*, 293.
(9) Liu, E. K.; Davison, R. R. *J. Chem. Eng. Data* **1981**, *26*, 85.
(10) Kehlalan, H. V.; Groller, J.-P. E.; Benson, G. C. *J. Chim. Phys. Phys.-Chim. Biol*. **1978**, *75*, 1031.
(11) Bondi, A. "Physical Properties of Molecular Crystals, Liquids and Glasses"; Wiley: New York, 1968.

Vapor Pressures of Binary (H₂O–HCl, –MgCl₂, and –CaCl₂) and Ternary (H₂O–MgCl₂–CaCl₂) Aqueous Solutions

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Vapor pressures of binary aqueous solutions containing HCl (1.262–13.435 mol/kg), MgCl₂ (1.051–4.104 mol/kg), and CaCl₂ (0.9568–5.002 mol/kg) were measured from 320 to 400 K. Furthermore, those of a ternary solution containing both MgCl₂ (1.057 mol/kg) and CaCl₂ (2.905 mol/kg) were also measured in the same temperature range. The apparatus for measuring vapor pressures was an all-glass Bourdon gauge and the precision of measurement was ±0.1 K or ±70 Pa, whichever was larger. The experimental data for the binary solutions were fitted to the Antoine type of equation adapted to concentrated aqueous solution and were in good agreement with the calculated results for all solutions. On the other hand, the data obtained for the ternary solution were compared with the values estimated by Teruya's method, and they both agreed well.

Introduction

Vapor pressure data of aqueous electrolyte solutions are important for the study of salt effects on vapor–liquid equilibrium. Data for a lot of aqueous electrolyte solutions are available in the literature (1, 2) and the correlation methods (3–5) have also been reported. In this work, the vapor pressures of three binary (H₂O–HCl, –MgCl₂, and –CaCl₂) solutions and one ternary (H₂O–MgCl₂–CaCl₂) solution were measured by using an all-glass Bourdon gauge which was more accurate than that used previously for MgI₂ solution (6). The results were correlated by the Antoine type of equation.

Experimental Section

Apparatus and Procedure. Vapor pressure was measured by using an all-glass Bourdon gauge similar to that devised by

Ewing (7). The form of the gauge is shown in Figure 1. It consisted of a thin-walled glass spiral (A), a pointer 25 cm in length (B), an outer tube 7 cm in diameter (C), a sample container with a volume of about 30 cm³ (D), and a connecting tube of 0.25-cm inside diameter (F). The sensitivity of the gauge was 40 Pa. The volume occupied by the vapor phase was made as small as possible to minimize the change of liquid-phase composition due to distribution of water or HCl between both phases. For this apparatus in which the volume of the liquid phase was about 25 cm³ and that of the vapor phase was about 10 cm³, the change of the composition was negligible (within 0.1%). The temperature was measured within ±0.1 K with a platinum resistance thermometer (E) calibrated against a standard thermometer. A mercury manometer readable to 13.3 Pa and a cylinder of nitrogen gas were connected ahead of tube G. The temperature of the air bath (H) was controlled to within ±0.1 K.

Before each run, the extraneous gas in the solution and apparatus was removed by use of a vacuum pump for 15 min at room temperature. The vapor pressure of a sample was determined by measuring the pressure outside of the spiral which was equal to the vapor pressure inside of the spiral. The position of the pointer in balance of the pressure on both sides was observed by means of a cathetometer. To examine the consistency of the apparatus, the vapor pressures of pure water were measured and they agreed well with the literature values (8) (the maximum deviation was 213 Pa at 387.6 K and the mean deviation was 67 Pa).

Materials and Analysis. HCl, MgCl₂, and CaCl₂ used in this work were of guaranteed reagent grade from Wacô Chemicals Co., and all the reagents were used without further purification. Water, which was deionized and distilled, was used throughout the experimental work.

The composition of the sample was analyzed after vapor pressure measurement. HCl was analyzed by acid–base titra-