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Excess Volumes of Binary Mixtures of *n*-Heptane with Hexane Isomers[†]

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Dilatometric measurements of excess volumes are described for binary mixtures of *n*-heptane with the five isomeric hexanes at 298.15 K. The results are compared with those of other investigators and are correlated with previously reported excess enthalpies by means of the Flory theory of mixtures.

Currently our laboratory is studying the variations in the excess thermodynamic properties of binary mixtures which result from isomeric changes in one of the components. Recently we reported (*1*) molar excess enthalpies for binary mixtures of *n*-heptane with the five isomeric hexanes: *n*-hexane (n-C6), 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB). As an extension of that work, we have measured molar excess volumes at 298.15 K for the same set of mixtures.

Experimental Section

The samples of *n*-heptane and the hexane isomers were the same as used in our calorimetric work (*1*). Molar excess volumes V_m^E were measured at 298.15 K and atmospheric pressure in the successive dilution micrometer syringe dilatometer described by Tanaka et al. (*2*). The errors of V_m^E and of the *n*-heptane mole fraction x are estimated to be less than $0.0003 + 0.001|V_m^E|$ cm^3 mol^{-1} and 5×10^{-5}, respectively.

Results and Discussion

The experimental values of V_m^E are listed in Table I. The method of least squares with all points assigned unit weight was used to fit the form

$$V_m^E = x(1-x)\sum_{j=1}^{n} v_j(1-2x)^{j-1} \qquad (1)$$

to each set of results. Values of the coefficients v_j and the standard deviations σ for these representations are summarized in Table II. Plots of the experimental results and of their representations by eq 1 are given in Figure 1.

Densities of binary mixtures of *n*-heptane with n-C6 at 293.15 K were reported by Loiseleur et al. (*3*). These lead to negative values of the molar excess volume (−0.08 cm^3 mol^{-1} for an equimolar mixture) which are larger in magnitude than our results (−0.0280 cm^3 mol^{-1} for an equimolar mixture), and it is unlikely that the differences can be attributed to the difference in the temperatures of the two studies. More recently, V_m^E at 298.15 K has been reported for mixtures of *n*-heptane with n-C6 (*4*) and with 2,3-DMB (*5*). Deviations between the results of these previous investigations and our findings are shown in Figure 2. There is agreement within ~0.001 cm^3 mol^{-1} between our results for the n-C6 system and those of Goates et al. (*4*). However, the latter show more scatter and tend to be higher (i.e., less negative) than our results for $x < 0.5$ and lower (i.e., more negative) than our results for $x > 0.5$. Larger deviations are evident between the two sets of results for the 2,3-DMB system. The data of Grolier and Faradjzadeh (*5*) are more skewed toward low x values, and for $x = 0.3$ are ~0.004 cm^3 mol^{-1} higher than our findings.

The magnitudes of V_m^E for the five systems in Figure 1 decrease in the following order:

$$\text{2,2-DMB} > \text{2-MP} > \text{2,3-DMB} > \text{n-C6} > \text{3-MP} \qquad (2)$$

This differs from the order of the excess enthalpy curves (*1*) and is closer to, although not identical with, the order of the V_m^E curves for mixtures of 1-hexanol with the hexane isomers (*6*). In the latter case, we noted that V_m^E (0.5) for equimolar mixtures varied nearly linearly with the solubility parameter of the isomer (coefficient of correlation $r = 0.977$). Since then we have examined correlations between the values of $V_m^E(0.5)$ and several other physical properties or configurational parameters of the isomers. These include the internal pressure, molar energy of vaporization, isothermal compressibility, number of gauche conformations, and third-order connectivity. The best correlation is shown in Figure 3, where there is a nearly linear variation of $V_m^E(0.5)$ with the isothermal compressibility κ_T of the pure hexane isomer for both the present *n*-heptane mixtures and the previous 1-hexanol mixtures (*6*) with $r = 0.994$ and 0.995, respectively.

The negative excess volumes and positive excess enthalpies (*1*) of *n*-heptane–hexane isomer mixtures are in disagreement

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Table I. Experimental Results for the Molar Excess Volume, V_m^E, of *n*-Heptane–Hexane Isomer Mixtures at Mole Fraction, x, of *n*-Heptane and 298.15 K

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-Heptane–n-C6				
0.011 55	−0.0014	0.305 42	−0.0243	0.501 46	−0.0279	0.772 25	−0.0182
0.033 71	−0.0038	0.356 64	−0.0263	0.502 14	−0.0281	0.825 13	−0.0145
0.065 33	−0.0071	0.400 70	−0.0274	0.540 66	−0.0274	0.871 57	−0.0112
0.104 33	−0.0108	0.438 50	−0.0280	0.586 75	−0.0262	0.918 77	−0.0074
0.141 67	−0.0143	0.439 01	−0.0281	0.641 35	−0.0247	0.957 84	−0.0040
0.188 68	−0.0180	0.467 67	−0.0281	0.707 52	−0.0219	0.985 60	−0.0015
0.245 18	−0.0215	0.472 55	−0.0282				
			n-Heptane–2-MP				
0.011 89	−0.0035	0.307 82	−0.0596	0.502 27	−0.0666	0.773 16	−0.0434
0.034 33	−0.0098	0.359 22	−0.0637	0.505 03	−0.0668	0.827 72	−0.0350
0.066 25	−0.0184	0.403 38	−0.0658	0.541 55	−0.0655	0.871 71	−0.0271
0.105 51	−0.0277	0.438 94	−0.0668	0.587 56	−0.0631	0.918 86	−0.0176
0.142 99	−0.0354	0.441 66	−0.0671	0.642 36	−0.0591	0.957 78	−0.0096
0.190 41	−0.0442	0.468 36	−0.0669	0.709 22	−0.0521	0.985 45	−0.0035
0.247 26	−0.0528	0.475 34	−0.0670				
			n-Heptane–3-MP				
0.011 67	−0.0012	0.307 73	−0.0223	0.494 55	−0.0255	0.767 44	−0.0169
0.034 13	−0.0034	0.359 16	−0.0241	0.505 08	−0.0256	0.822 95	−0.0136
0.066 08	−0.0066	0.403 34	−0.0251	0.534 06	−0.0251	0.868 09	−0.0105
0.105 42	−0.0101	0.431 22	−0.0255	0.580 22	−0.0243	0.916 40	−0.0068
0.142 88	−0.0129	0.441 73	−0.0256	0.635 38	−0.0225	0.956 35	−0.0037
0.190 24	−0.0163	0.460 49	−0.0256	0.702 56	−0.0201	0.984 66	−0.0014
0.247 10	−0.0194	0.475 36	−0.0257				
			n-Heptane–2,2-DMB				
0.011 70	−0.0068	0.309 16	−0.1255	0.505 85	−0.1431	0.777 41	−0.0945
0.034 19	−0.0195	0.360 67	−0.1353	0.508 81	−0.1432	0.830 66	−0.0761
0.066 26	−0.0367	0.404 76	−0.1400	0.547 98	−0.1410	0.874 79	−0.0591
0.105 69	−0.0563	0.442 96	−0.1425	0.593 95	−0.1361	0.920 81	−0.0390
0.143 72	−0.0731	0.445 70	−0.1429	0.648 40	−0.1268	0.958 81	−0.0215
0.191 09	−0.0917	0.475 02	−0.1437	0.714 20	−0.1127	0.985 88	−0.0077
0.248 37	−0.1101	0.476 43	−0.1434				
			n-Heptane–2,3-DMB				
0.011 71	−0.0024	0.306 70	−0.0472	0.501 21	−0.0551	0.771 93	−0.0372
0.034 07	−0.0070	0.358 03	−0.0510	0.503 85	−0.0555	0.823 46	−0.0306
0.065 76	−0.0133	0.402 11	−0.0535	0.540 53	−0.0546	0.870 97	−0.0237
0.104 95	−0.0207	0.437 92	−0.0548	0.586 64	−0.0527	0.918 27	−0.0158
0.142 36	−0.0272	0.440 36	−0.0545	0.641 44	−0.0494	0.957 46	−0.0088
0.189 54	−0.0339	0.467 31	−0.0550	0.707 87	−0.0441	0.985 43	−0.0032
0.246 22	−0.0411	0.474 26	−0.0555				

Table II. Coefficients, v_j, and Standard Deviation, σ, for Representations of V_m^E by Eq 1

	hexane isomer				
	n-C6	2-MP	3-MP	2,2-DMB	2,3-DMB
v_1	−0.11188	−0.26683	−0.10208	−0.57305	−0.22075
v_2	−0.01193	−0.03372	−0.01038	−0.04847	−0.01323
v_3	0.00657		0.00677	0.01189	0.02139
v_4				0.02161	0.01259
v_5					−0.02008
σ	0.00015	0.00013	0.00014	0.00021	0.00017

with simple regular solution theory (*7*), which predicts that these quantities should be of the same sign. Recently Tra Van and Patterson (*8*) have reported that excess volume data for hexane isomers with *n*-hexadecane and with a highly branched hexadecane isomer can be interpreted on the basis of a corresponding states formulation of the Flory theory (*9*), which recognizes equation of state contributions in addition to those associated with the interchange energy.

It appears that a semiquantitative interpretation of our results is possible in terms of the Flory theory of mixtures in its original form (*10*, *11*). The formulas used in our treatment have been outlined several times (*12*, *13*) and will not be repeated here. A summary of the calculations is given in Table III. This lists the values and sources for the molar volumes V_m (*1*, *16*), isobaric thermal expansivities α_p (*14*, *18*), and isothermal

Table III. Component Properties and Parameters Used in Calculations for *n*-Heptane (1)–Hexane Isomer (2) Mixtures at 298.15 K by the Flory Theory

	V_m/ (cm^3 mol^{-1})	α_p/kK^{-1}	κ_T/TPa^{-1}	p^*/ (J cm^{-3})	v^*/ (cm^3 mol^{-1})	T^*/K	s_{12}	X_{12}/ (J cm^{-3})
C_7H_{16}	147.45[a]	1.256[b]	1460.6[c]	431.9	113.60	4648.1		
n-C6	131.57[d]	1.387[b]	1703.9[e]	424.2	99.52	4436.1	0.9569	0.1097
2-MP	132.89[d]	1.426[f]	1838.9[g]	408.3	99.99	4380.8	0.9584	0.6041
3-MP	130.61[d]	1.396[f]	1719.1[g]	424.2	98.68	4423.0	0.9541	0.4880
2,2-DMB	133.73[d]	1.468[f]	2009.6[g]	389.0	100.07	4324.8	0.9586	1.0346
2,3-DMB	131.16[d]	1.391[f]	1790.2[g]	405.3	99.16	4430.2	0.9557	0.4435

[a] From density in ref *1*. [b] Reference *14*. [c] From speed of sound and other data in ref *15*. [d] From density in ref *16*. [e] From speed of sound and other data in ref *17*. [f] Estimated from density in ref *18*. [g] From speed of sound and other data in ref *19*.

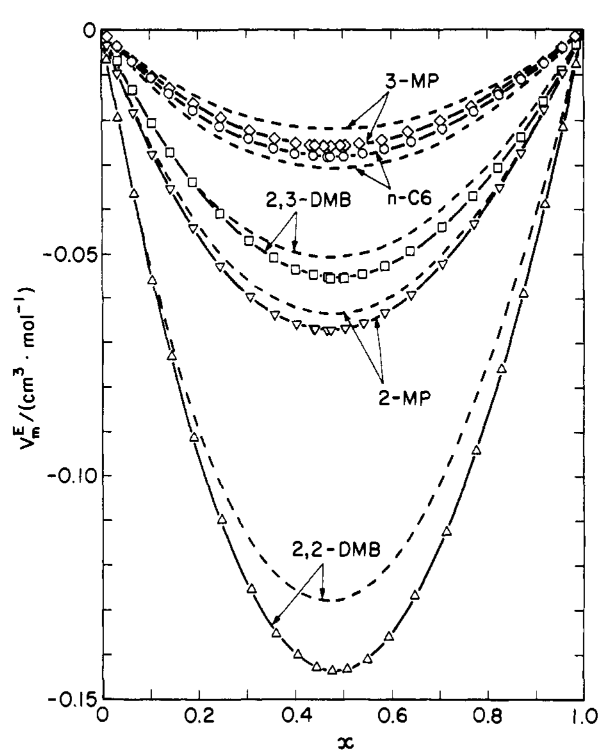

Figure 1. Molar excess volume, V_m^E, of *n*-heptane–isomeric hexane mixtures at mole fraction, x, of *n*-heptane and 298.15 K: (○) n-C6; (▽) 2-MP; (◇) 3-MP; (△) 2,2-DMB; (□) 2,3-DMB. Curves: (—) calculated from eq 1; (– – –) calculated from Flory theory.

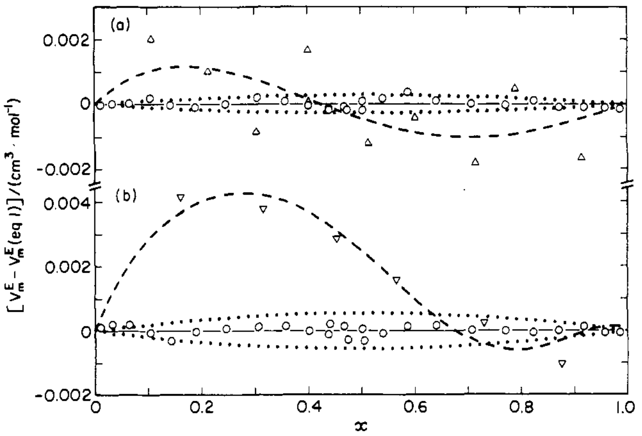

Figure 2. Deviation of molar excess volume from eq 1, $V_m^E - V_m^E$(eq 1), for some *n*-heptane–hexane isomer mixtures at mole fraction x of *n*-heptane and 298.15 K. Curves: (···) indicate deviations of ±1%. (a) Mixture with n-C6: (○) our experimental results; (△, – – –) Goates et al. (*4*). (b) Mixture with 2,3-DMB: (○) our experimental results; (▽, – – –) Groller and Faradjzadeh (*5*).

compressibilities κ_T (*15*, *17*, *19*) of the pure components and gives the values derived for their characteristic pressures p^*, molar volumes v^* and temperatures T^*. For each mixture, the ratio of molecular surface areas of contact s_{12} was estimated from the characteristic volumes, assuming the molecules to be approximately spherical, and the interchange energy X_{12} was determined to give a least-squares fit between the calculated and experimental (*1*) excess enthalpy curves. The values obtained for s_{12} and X_{12} are also listed in Table III. Values of V_m^E estimated according to the Flory theory with the parameters given in Table III are shown as broken curves in Figure 1. For all the isomers except n-C6, the theory slightly underestimates the magnitude of V_m^E. However, bearing in mind the simplifying assumptions of the treatment, the agreement with experiment is excellent, and it is particularly gratifying that the correct order of the curves is predicted.

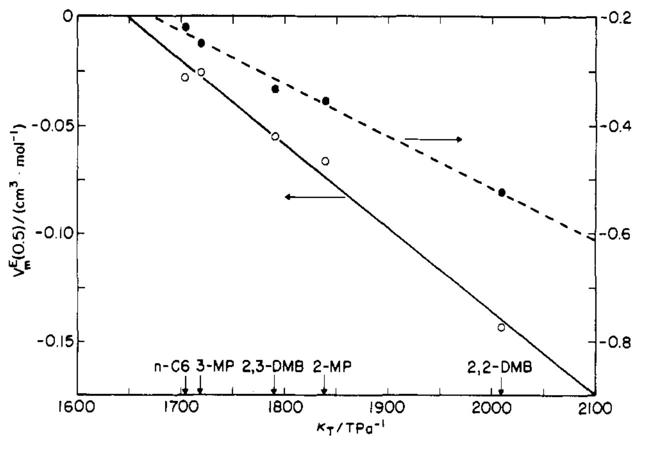

Figure 3. Plot of $V_m^E(0.5)$, the molar excess volume of an equimolar mixture of either *n*-heptane or 1-hexanol with the five isomeric hexanes at 298.15 K, against κ_T, the isothermal compressibility of the hexane isomer (values and sources given in Table III): (○) present results for *n*-heptane mixtures; (●) 1-hexanol mixtures from ref *6*; (—, – – –) least-squares lines with coefficients of correlation = 0.994 and 0.995, respectively.

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Glossary

n	number of coefficients in eq 1
p^*	characteristic pressure in Flory theory, J cm^{-3}
r	coefficient of correlation
s_{12}	ratio of molecular surface areas of contact in Flory theory
T^*	characteristic temperature in Flory theory, K
v_i	coefficient in eq 1
v^*	characteristic molar volume in Flory theory, cm^3 mol^{-1}
V_m	molar volume, cm^3 mol^{-1}
V_m^E	molar excess volume, cm^3 mol^{-1}
x	mole fraction of component 1 in mixture
X_{12}	interchange energy parameter in Flory theory, J cm^{-3}

Greek Letters

α_p	isobaric thermal expansivity, kK^{-1}
κ_T	isothermal compressibility, TPa^{-1}
σ	standard deviation for least-squares fit of V_m^E, cm^3 mol^{-1}

Subscripts

1	component 1, *n*-heptane
2	component 2, hexane isomer

Registry No. *n*-C6, 110-54-3; 2-MP, 107-83-5; 3-MP, 96-14-0; 2,2-DMB, 75-83-2; 2,3-DMP, 79-29-8; *n*-heptane, 142-82-5.

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Solubility Relations in the Ternary System NaCl–CsCl–H_2O at 1 atm. 1. Solubilities of Halite from 20 to 100 °C

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Solubilities of halite in the ternary system NaCl–CsCl–H_2O have been determined by the visual polythermal method at 1 atm from 20 to 100 °C along five constant CsCl/(CsCl + H_2O) weight ratio lines. These five constant weight ratios are 0.1, 0.2, 0.3, 0.4, and 0.5. The maximum uncertainties in these measurements are ±0.02 wt % NaCl and ±0.15 °C. The data along each constant CsCl/(CsCl + H_2O) weight ratio line were regressed to a smooth curve. The maximum deviation of the measured solubilities from the smooth curves is 0.06 wt % NaCl. Isothermal solubilities of halite were calculated from these smoothed curves at 25, 50, and 75 °C.

Introduction

^{137}Cs is a significant producer of both heat and radioactivity for about 100 years in high-level radioactive waste (*1*). Since a committee of geologists in The National Academy of Sciences–National Research Council studied the problem (*2*) in 1955, natural salt deposits, either in bedded or domal forms, have been considered as promising candidates for the terminal storage sites for high-level wastes. Knowledge of solubility relations in the system NaCl–CsCl–H_2O is essential for the assessment and eventual solution of problems related to the leaching and the subsequent migration of the ^{137}Cs radionuclide in salt repositories.

Plyushchev et al. (*3*) determined the solubility relations in the system NaCl–CsCl–H_2O at 25, 50, and 75 °C, using the isothermal method. Na^+ and Cl^- concentrations in the equilibrated solutions were determined gravimetrically while the concentration of Cs^+ was calculated by difference. Since the bulk composition and the final solution composition were known, the composition of the solid phases was determined by using the Schreinemaker residue method.

The solubility data of Plyushchev et al. (*3*) at 25, 50, and 75 °C are shown in Figure 1 with the coexisting solid phases omitted for clarity. The crossover of the isotherms indicates the poor quality of the data. The present paper reports the solubilities of halite in the ternary system NaCl–CsCl–H_2O from 20 to 100 °C at 1 atm. Solubility relations in the CsCl-rich region of this system at 25, 50, and 75 °C will be presented in subsequent papers in this series.

Experimental Section

The visual polythermal method used in this study has been discussed in detail previously (*4*, *5*). Solubilities of halite have been determined between 20 and 100 °C along the five constant CsCl/(CsCl + H_2O) weight ratio lines, BD, BE, BF, BG, and BH shown in Figure 2. The solid phase involved in these solubility measurements is halite as indicated by the data of Plyushchev et al. (*3*), Chou et al. (*6*), and Chou and Romankiw (*7*). As an example for the composition line BF, a sample (~ 12 g) was prepared by mixing weighed amounts of NaCl and a stock solution of 30 wt % CsCl (point F in Figure 2) in a Pyrex tube containing a magnetic stirring bar. A layer of silicone oil (~ 1 cm) was added to seal the tube and prevent water gain or loss. The assembly was mounted in a glycol bath, as shown in Figure 3, and incrementally heated and vigorously agitated until the last crystal was dissolved. Heating increments were made progressively smaller as the amount of salt decreases. The temperature (read to ±0.1 °C with a calibrated platinum resistance thermometer) at which the last salt crystal disappeared was taken as the equilibrium temperature for the bulk composition in the tube. Experiments showed that 1 mg of salt could easily be seen with the unaided eye. Once the last crystal dissolved, the solution had to be significantly supercooled to induce crystallization. This precludes the possibility of reversing the solubility data by simple cooling. However, the equilibrium between crystals and solution in the heating experiments has been sufficiently demonstrated (*4*).

Results and Discussion

The measured halite solubilities along the five constant CsCl/(CsCl + H_2O) weight ratio lines are listed in Table I together with smoothed values and the deviation of the measured values from the smoothed results. The maximum uncertainties in these measurements are ±0.15 °C. The smoothed values were obtained from a least-squares regression of the experimental values to an equation of the form

$$S = \sum_{0}^{i} a_i t^i \qquad (1)$$

where S is the solubility in grams of NaCl per 100 g of saturated solution (g/100 g), and t is the temperature in degrees Celsius. The coefficients, a_i, for the regression equation are listed in