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Thermodynamics of Liquid Mixtures Containing Hydrocarbons and Strongly Polar Substances: V^{E} and $C_{\mathrm{p}}^{\mathrm{E}}$ of {Pyridine or Piperidine + Cyclohexane} at 298.15 K

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Summary. Excess molar volumes V^{E} and excess molar heat capacities $C_{\mathrm{p}}^{\mathrm{E}}$ at constant pressure have been determined, as a function of mole fraction x_1 at 298.15 K and atmospheric pressure, for the two liquid mixtures {pyridine or piperidine + cyclohexane}. The instruments used were a vibrating-tube densimeter and a Picker flow microcalorimeter, respectively. The two systems show positive excess volumes with $V^{\mathrm{E}}(x_1 = 0.5) = 0.531\,\mathrm{cm^3 \cdot mol^{-1}}$ for {pyridine + cyclohexane} and $0.295\,\mathrm{cm^3 \cdot mol^{-1}}$ for {piperidine + cyclohexane}. The curve $C_{\mathrm{p}}^{\mathrm{E}}$ *vs.* x_1 for {pyridine + cyclohexane} shows a rather complex S-shape: $C_{\mathrm{p}}^{\mathrm{E}}$ is negative at small mole fractions x_1 of pyridine and positive for $x_1 > 0.22$, roughly. $C_{\mathrm{p}}^{\mathrm{E}}$ of the piperidine system is negative throughout and strongly asymmetric with the minimum $C_{\mathrm{p}}^{\mathrm{E}}(x_{1,\mathrm{min}}) = -2.32\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ being situated at a mole fraction of piperidine $x_{1,\mathrm{min}} \approx 0.27$.

Keywords. Thermodynamics; Excess molar volume; Excess molar heat capacity; Liquid mixtures; Density; Calorimetry; Pyridine; Piperidine; Cyclohexane.

Zur Thermodynamik flüssiger Mischungen von Kohlenwasserstoffen und stark polaren Substanzen: V^{E} und $C_{\mathrm{p}}^{\mathrm{E}}$ von {Pyridin oder Piperidin + Cyclohexan} bei 298.15 K

Zusammenfassung. Für die beiden flüssigen Mischungen {Pyridin oder Piperidin + Cyclohexan} wurden molare Zusatzvolumina V^{E} und molare Zusatzwärmekapazitäten $C_{\mathrm{p}}^{\mathrm{E}}$ bei konstantem Druck als Funktion des Molenbruchs x_1 bei 298.15 K bestimmt. Die Messungen wurden mit einem Biegeschwinger-Dichtemeßgerät bzw. einem Strömungsmikrokalorimeter nach Picker durchgeführt. Die Zusatzmolvolumina beider Systeme sind positiv mit $V^{\mathrm{E}}(x_1 = 0.5) = 0.531\,\mathrm{cm^3 \cdot mol^{-1}}$ für {Pyridin + Cyclohexan} und $0.295\,\mathrm{cm^3 \cdot mol^{-1}}$ für {Piperidin + Cyclohexan}. Die Kurve $C_{\mathrm{p}}^{\mathrm{E}}$ *vs.* x_1 des Systems {Pyridin + Cyclohexan} zeigt einen ungewöhnlichen S-förmigen Verlauf: bei kleinen Molenbrüchen x_1 von Pyridin ist $C_{\mathrm{p}}^{\mathrm{E}}$ negativ, für $x_1 > 0.22$ ist $C_{\mathrm{p}}^{\mathrm{E}}$ positiv. Die molare Zusatzwärmekapazität des Piperidinsystems ist überall negativ und stark unsymmetrisch: im Minimum bei $x_{1,\mathrm{min}} \approx 0.27$ findet man $C_{\mathrm{p}}^{\mathrm{E}}(x_{1,\mathrm{min}}) = -2.32\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

Introduction

Recent experimental work on thermodynamic properties of binary liquid mixtures of type {polar substance + hydrocarbon} has revealed surprisingly different and sometimes quite unexpected mixing behaviors, [1–17], such as a W-shaped composition dependence of the excess molar heat capacity C_p^E at constant pressure. Results on the first systems showing this composition dependence, that is on {1,4-dioxane + n-heptane or n-decane or n-tetradecane} were reported by us in 1982 at the 37th Annual Calorimetry Conference in Snowbird, USA [4]. Since then, the number of mixtures known to show such W-shaped curves has increased steadily. This behavior is now recognized as being of relatively wide occurrence in liquid mixtures of the composition {strongly polar substance + alkane}, although it is not restricted to this kind of systems. Our systematic studies have involved both protic and aprotic (without hydrogen bonds) polar substances. In particular, a recent comparative study has been devoted to the two series {pyridine + *n*-alkane} and {piperidine + *n*-alkane} [15]. Some systems belonging to the former series show C_p^E curves with two minima and one maximum, *i.e.* W-shaped curves. As a sequel we present here excess molar volumes V^E and excess molar heat capacities C_p^E at temperature $T = 298.15$ K and atmospheric pressure of the two binary liquid mixtures {pyridine (C_5H_5N) + cyclohexane (c–C_6H_{12})} and {piperidine ($C_5H_{10}NH$) + cyclohexane}. These polar liquids have been selected for the following reasons: both pyridine and piperidine are six-membered heterocycles of comparable size, yet pyridine is considerably more polar. Further, pyridine is an aprotic solvent, while piperidine is protic.

Experimental

Materials

All liquids, that is pyridine, piperidine and cyclohexane, were *puriss. p.a.* quality from Fluka with purities exceeding 99.8 mol %, 99 mol % and 99.5 mol %, respectively. They were carefully dried with a molecular sieve (Union Carbide Type 4A, beads, from Fluka) and used without further purification.

Mixtures for both V^E and C_p^E determinations were prepared by mass with a possible error in the mole fractions estimated to be less than 10^{-4}. All molar quantities are based on the relative atomic mass table of IUPAC 1991 [18].

Procedures

Excess volumes: Densities ρ were measured with a vibrating-tube densimeter [19] from Sodev, which was operated under flow conditions. Before each series of measurements the instrument was calibrated with vacuum and doubly distilled and degassed water, using ρ_{H_2O} (298.15 K) = 0.997047 g·cm^{-3} as reported by Kell. [20]. The density ρ of any liquid relative to the density of pure water ρ_{H_2O} is given by

$$\rho = \rho_{H_2O} + K(\tau^2 - \tau_{H_2O}^2), \qquad (1)$$

where K is a temperature-dependent constant characteristic of a particular oscillator, and τ and τ_{H_2O} are the periods of vibration of the tube filled with the liquid and with water, respectively. They were measured with a high-resolution digital frequency meter from Schneider. Temperature control by the thermostat was better than ±0.002 K as checked by a quartz thermometer. The maximum inaccuracy of the temperature readings is estimated to be less than ±0.005 K.

From the measured densities of the mixtures, the excess molar volumes were obtained via

$$V^{E} = V - (x_1 V_1^* + x_2 V_2^*) = x_1 M_1 (1/\rho - 1/\rho_1^*) + x_1 M_2 (1/\rho - 1/\rho_2^*), \tag{2}$$

where V_i^*, M_i, ρ_i^*, and x_i denote, respectively, the molar volume, the molar mass, the density, and the mole fraction of either pyridine or piperidine ($i = 1$), or of cyclohexane ($i = 2$), and V is the molar volume of the mixture, *i.e.*

$$V = (x_1 M_1 + x_2 M_2)/\rho. \tag{3}$$

Excess heat capacities: Heat capacities divided by volume, C_P/V, were measured with a Picker flow microcalorimeter (from Setaram) using the stepwise procedure [19, 21, 22]. With this procedure, the mixtures are studied in the order of increasing mole fraction of one component. Starting with, say, pure liquid cyclohexane (component 2), each mixture is used as a reference for the subsequent mixture in the series until pure component 1 (either pyridine or piperidine) is reached. Thus, for the k^{th} mixture

$$(C_P/V)_k = (C_{P,2}^*/V_2^*) \prod_{j=1}^{k} (1 + \Delta W_j/W), \tag{4}$$

where C_P is the molar heat capacity at constant pressure of the mixture having a molar volume V, and $C_{P,2}^*$ is the molar heat capacity at constant pressure of pure cyclohexane. The initial heating power applied to both the measuring and the reference cell (ca. 20 mW) is denoted by W, and ΔW_j is the change in power supplied by the thermal feedback circuit to keep the temperature gradients equal in both cells. Before entering the cells, the liquids were thermostatted to better than ± 0.002 K as checked by a quartz thermometer. For all measurements we used a temperature increment of approximately 1 K centered on 298.15 K. Fluka *puriss.* n-heptane was used as ultimate reference liquid: a value of 224.78 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was adopted for its molar heat capacity at 298.15 K [23]. The heat capacities divided by volume were converted to molar heat capacities with use of our measured densities. Excess molar heat capacities were then calculated from

$$C_P^E = C_P - (x_1 C_{P,1}^* + x_2 C_{P,2}^*), \tag{5}$$

where $C_{P,1}^*$ is the molar heat capacity at constant pressure of pure liquid component 1, *i.e.* either of pyridine or of piperidine.

Results and Discussion

Experimental densities and molar heat capacities of the pure liquids are given in Table 1 along with reliable values from the literature. Agreement with the literature data is satisfactory throughout.

Results for the excess molar volumes and the excess molar heat capacities of the three mixtures studied at 298.15 K are given in Table 2, while graphical representations are provided by Figs. 1 and 2. For each mixture, the experimental excess quantities were fittered with a smoothing function of *Redlich–Kister* type

$$Q^E = x_1 x_2 \sum_{i=0}^{k} A_i (x_1 - x_2)^i, \tag{6}$$

where $Q^E = V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$ or $Q^E = C_P^E/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$. The parameters A_i and the corresponding standard deviations $s(Q^E)$ are shown in Table 3. These parameters were used to obtain the calculated curves in the figures.

The volumetric behavior of $\{x_1 C_5H_5N + x_2 c\text{–}C_6H_{12}\}$ at 298.15 K has been investigated by *Woycicki* and *Sadowska* [34], *Brzostowski et al.* [35], *Kowalski et al.* [36], and *Weclawski* [37]. Agreement with the results of the former two groups

Table 1. Densities ρ^* and molar heat capacities C_p^* at constant pressure of the pure liquids at 298.15 K

Substance	ρ^* (g·cm^{-3})		C_p^* (J·K^{-1}·mol^{-1})	
	this work	literature	this work	literature
Pyridine (C_5H_5N)	0.97794	0.97824[a], 0.97812[b], 0.97810[c]	131.33	132.74[i], 131.47[j]
Piperidine ($C_5H_{10}NH$)	0.85685	0.85691[d], 0.85680[e], 0.85674[f]	177.41	182.81[e], 179.95[k], 177.62[j]
Cyclohexane (c–C_6H_{12})	0.77375 0.77367	0.77389[f], 0.77384[g], 0.77370[h]	156.89 156.68	156.35[l], 156.07[m], 156.01[g]

[a] Ref. [24]; [b] Ref. [25]; [c] Ref. [26]; [d] Ref. [27]; [e] Ref. [28]; [f] Ref. [29]; [g] Ref. [30]; [h] Ref. [31]; [i] Ref. [32]; [j] Ref. [15]; [k] Ref. [33]; [l] Ref. [19]; [m] Ref. [23]

Table 2. Excess molar volumes V^E and excess molar heat capacities C_p^E for {pyridine + cyclohexane} and {piperidine + cyclohexane} at 298.15 K and atmospheric pressure

x_1	V^E(cm^3·mol^{-1})	C_p^E(J·K^{-1}·mol^{-1})	x_1	V^E(cm^3·mol^{-1})	C_p^E(J·K^{-1}·mol^{-1})
$\{x_1C_5H_5N + x_2c\text{–}C_6H_{12})\}$					
0.0737	0.2418	−0.362	0.5901	0.4679	0.633
0.1412	0.3905	−0.282	0.6999	0.3518	0.516
0.2156	0.4923	−0.031	0.7746	0.2671	0.402
0.2977	0.5518	0.284	0.8492	0.1810	0.343
0.3976	0.5671	0.558	0.9215	0.0916	0.216
0.4961	0.5328	0.657			
$\{x_1C_5H_{10}NH + x_2c\text{–}C_6H_{12})\}$					
0.0797	0.1244	−1.352	0.6016	0.2640	−1.309
0.1578	0.2060	−2.055	0.6991	0.2203	−0.900
0.2302	0.2556	−2.301	0.7763	0.1763	−0.607
0.3004	0.2853	−2.266	0.8495	0.1276	−0.355
0.4092	0.3023	−2.049	0.9221	0.0742	−0.111
0.5021	0.2946	−1.696			

Table 3. *Redlich–Kister* parameters A_i and standard deviations $\sigma(Q^E)$ for least-squares representation of excess molar quantities Q^E at 298.15 K and atmospheric pressure by eq. (6)

Mixture	Q^E	A_0	A_1	A_2	A_3	A_4	$\sigma(Q^E)$
$\{x_1C_5H_5N + x_2c\text{–}C_6H_{12}\}$	V^E	2.1236	−1.1310	0.2186	−0.2841	0.2297	0.001_5
	C_p^E	2.713	0.220	−5.142	6.405		0.01_5
$\{x_1C_5H_{10}NH + x_2c\text{–}C_6H_{12}\}$	V^E	1.1783	−0.3939	0.1070	−0.0054	0.2187	0.000_6
	C_p^E	−6.879	7.710	−4.572	3.266		0.01_6

is excellent; the excess volumes reported by the latter two are slightly smaller than ours. Excess volumes of $\{x_1C_5H_{10}NH + x_2c\text{–}C_6H_{12}\}$ have been communicated by *Moelwyn-Hughes* and *Thorpe* (at 20 and 40 °C) [28], *Woycicki* and *Sadowska* [38], and *Roveillo* and *Gomel* [39] (these authors presented their results only in graphical form at, presumably, 298.15 K). The interpolated results of *Moelwyn-Hughes* and *Thorpe* are slightly below ours (by ca. 0.02 cm^3·mol^{-1} at equimolar composition), whereas the V^E given by *Woycicki* and *Sadowska*, and *Roveillo* and *Gomel* are slightly above ours by about 0.04 cm^3·mol^{-1} and 0.02 cm^3·mol^{-1} at $x_1 = 0.5$, respectively.

Heat capacity measurements have been reported in the literature only for $\{x_1C_5H_{10}NH + x_2c\text{–}C_6H_{12}\}$. *Moelwyn-Hughes* and *Thorpe* [28] give a single value at $x_1 = 0.5050$: $C_p^E = -2.2$ J·K^{-1}·mol^{-1} at 298.15 K (interpolated), which is more negative by about 0.5 J·K^{-1}·mol^{-1} than our result. Several authors [34, 38, 40–43], however, have determined excess molar enthalpies H^E at different temperatures, which information could be used, in principle, to obtain $C_p^E = (\partial H^E/\partial T)_{p,x_1}$. In essentially all cases, the accuracy of these data is insufficient to afford reliable excess

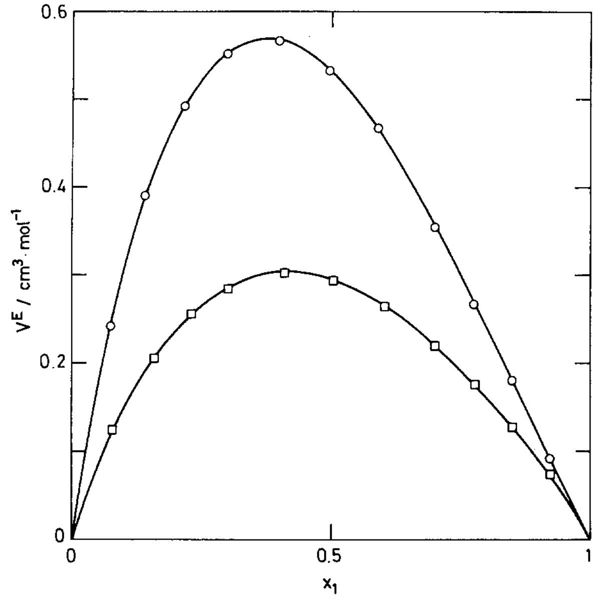

Fig. 1. Excess molar volumes V^E at 298.15 K. Experimental results: ○, $\{x_1C_5H_5N + x_2c\text{-}C_6H_{12}\}$; □, $\{x_1C_5H_{10}NH + x_2c\text{-}C_6H_{12}\}$. —, calculated with eq. (6) and parameters from Table 3.

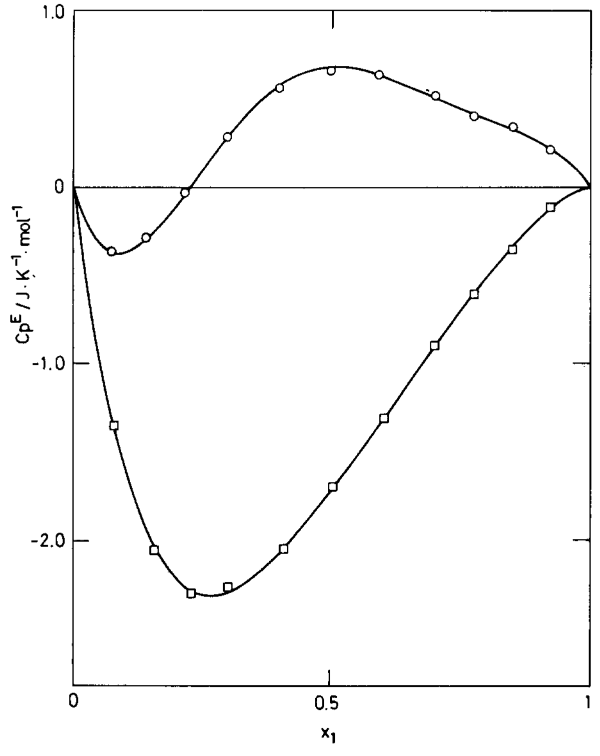

Fig. 2. Excess molar heat capacities C_p^E at constant pressure at 298.15 K. Experimental results: ○, $\{x_1C_5H_5N + x_2c\text{-}C_6H_{12}\}$; □, $\{x_1C_5H_{10}NH + x_2c\text{-}C_6H_{12}\}$. —, calculated with eq. (6) and parameters from Table 3.

molar heat capacities. For instance, C_p^E values so obtained for {pyridine + cyclohexane} from either Ref. [34], Ref. [41], or Ref. [43] are all negative and their absolute values are much too large. For {piperidine + cyclohexane}, only a single value for $x_1 = 0.5040$ at an average temperature of 290.65 K could be calculated from H^E data given in Ref. [38]: $C_p^E = -1.2\,J{\cdot}K^{-1}{\cdot}mol^{-1}$, which is less negative by about 0.5 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ than our result. No other literature values could be found for comparison.

The most interesting aspect of our work relates to the composition dependence of the excess molar heat capacities, which is remarkably different for the two mixtures. While C_P^E of {piperidine + cyclohexane} is negative and more or less parabolic (yet strongly asymmetric), C_P^E of {pyridine + cyclohexane} shows a much more complicated shape reminiscent of that observed in the series {pyridine + *n*-alkane} with the lower alkanes *n*-heptane and *n*-decane, respectively [15]. We note that for mixtures with *n*-tetradecane or *n*-hexadecane W-shaped curves are obtained [15]. Qualitatively, the observed differences in C_P^E *vs.* x_1 between {pyridine + cyclohexane} and {piperidine + cyclohexane} may be related to the differences in effective polarity $\tilde{\mu}$ defined by [2, 10–12, 44]

$$\tilde{\mu}^2 \equiv \mu^2 N_A/(4\pi\varepsilon_0 V_c k_B T_c), \tag{7}$$

yielding $\tilde{\mu}_{\mathrm{Pyr}}/\tilde{\mu}_{\mathrm{Pip}} = 2.56$ [15]. Here μ is the permanent electric dipole moment, V_c is the critical molar volume, T_c is the critical temperature, N_A is *Avogadro*'s constant, ε_0 is the permittivity of vacuum, and k_B is *Boltzmann*'s constant. As suggested previously [2, 12, 15, 45], C_P^E may be separated into random (r) and nonrandom (nr) contributions, the latter being associated with significant preferential orientation and aggregation between the strongly polar molecules. Using *Guggenheim*'s quasi-chemical theory [46] a rough approximation yields

$$\begin{aligned} C_P^E/R &= C_{P,r}^E/R + C_{P,nr}^E/R \\ &\approx -2x_1x_2b/(k_BT^2) + 2z^{-1}(H^E/RT)^2, \end{aligned} \tag{8}$$

where R is the gas constant, b characterizes the temperature dependence of *Guggenheim*'s free energy interchange parameter $w = a + b/T$ [47], and z is the lattice coordination number. The random term $C_{P,r}^E$ is negative, as expected for mixtures where dipolar or weak association order is being broken in the mixing process, whereas the non-random contribution $C_{P,nr}^E$ is positive. Thus, at 298.15 K and $x_1 = 0.5$, with $H^E = 1438\ \mathrm{J \cdot mol^{-1}}$ for {pyridine + cyclohexane} [34, 41–43, 48, 49] and $H^E = 827\ \mathrm{J \cdot mol^{-1}}$ for {piperidine + cyclohexane} [38, 50],

$$C_{P,nr}^E(\mathrm{Pyr + CH})/C_{P,nr}^E(\mathrm{Pip + CH}) \approx 3.0, \tag{9}$$

whence the different composition dependence of C_P^E of the two series may be rationalized [15]. Additional evidence comes from the *Kirkwood g* factor. Assuming that interaction is only considered between a molecule and its z nearest neighbors

$$g = 1 + z\langle\cos\gamma\rangle, \tag{10}$$

where γ is the angle between neighboring dipoles. This quantity has been determined for both series, [41, 48, 51] though in much greater detail for {pyridine + cyclohexane} [41]. For pure pyridine, $g \approx 0.9$, yet values substantially greater than 1 are observed in dilute solutions of pyridine. This may be taken as an indication of the existence of clusters of pyridine molecules exhibiting preferred parallel orientations. On the other hand, g of pure piperidine is slightly larger than 1 and diminishes gradually with increasing dilution [51]. Finally we note that for pyridine (relative dielectric permittivity $\varepsilon_r = 13.0$ at 298.15 K), the reduced *Trouton* constant

$\Delta S^0_{\text{vap}}(T_b)/R = 11.1$, whereas for piperidine ($\varepsilon_r = 4.3$ at 298.15 K) $\Delta S^0_{\text{vap}}(T_b)/R = 10.6$. [52].

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