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Vapor Pressure, Density, Refractive Index, Excess Enthalpy, and Heat Capacity of 2-Chloro-2-methylpropane or Chlorobenzene + 2,2,4-Trimethylpentane

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Excess volumes of the binary liquid mixtures of 2-chloro-2-methylpropane (*tert*-butyl chloride) or chlorobenzene + 2,2,4-trimethylpentane (isooctane) have been determined at 293.15 and 313.15 K from density measurements at atmospheric pressure. The excess enthalpies, at 293.15 K, and the excess isobaric heat capacities, at 293.15 K and 313.15 K, have been measured using Picker calorimeters at atmospheric pressure. Also the excess Gibbs energy of chlorobenzene + 2,2,4-trimethylpentane has been calculated from isothermal vapor–liquid equilibrium data at 303.15 and 323.15 K, taken in a dynamic Cottrell type apparatus, the equilibrium compositions being determined refractometrically.

Introduction

The measurements of the excess properties of 2-chloro-2-methylpropane (*tert*-butyl chloride) or chlorobenzene + 2,2,4-trimethylpentane (isooctane) presented here are part of a study on liquid mixtures of polar components (with different dipole moments) with a common nonpolar component, 2,2,4-trimethylpentane. References to other parts of this investigation have been summarized recently (*1*, *2*).

2-Chloro-2-methylpropane and chlorobenzene are the least polar fluids in the series studied with dipole moments in the gas phase of 2.13 and 1.70 D, leading to reduced dipole moments of 0.695 and 0.494 (*2*), respectively.

Experimental Section

Materials. 2-Chloro-2-methylpropane (EGA-Chemie, p. a.) with a purity of 98.80 mol % and chlorobenzene (Fluka, puriss.) with a purity of 99.98 mol %, both checked by GLC, were dried by storage over calcium chloride and over potassium carbonate, respectively (J. T. Baker Chemicals, Analytical Reagent). 2,2,4-Trimethylpentane (Fluka, puriss., or Phillips, Research Grade) with GLC purities of 99.97 or 99.98 mol %, respectively, was stored over Na-Pb (Merck, p. a.). The substances were used without further purification. They were carefully degassed by several pump/thaw cycles prior to each measurement. The molar quantities were calculated using the relative atomic masses according to IUPAC (1987) (*3*).

In Table I, the experimental densities ρ, the molar isobaric heat capacities C_p and, if measured, the vapor pressures p and the refractive indices n_D of the pure liquids are compared with literature data.

Apparatus and Procedure. Molar excess volumes V^E were calculated from precise density measurements of the liquids measured by means of a vibrating glass tube densimeter (Model DMA 02 D, Paar) at 293.15 and 313.15 K and atmospheric pressure. The precision in the densities is estimated as 3×10^{-6} g cm^{-3}, the accuracies are 2×10^{-5} g cm^{-3}, at 293.15 K, and 1×10^{-4} g cm^{-3}, at 313.15 K. V^E is accurate to 0.003 cm^3 mol^{-1} at about equimolar composition. Mixtures were prepared from the degassed samples under vacuum by weighing them into airtight screw-capped tubes; the masses were corrected for the gas phase. This led to accuracies in the mole fraction x_i of 3×10^{-5}. Details are given in ref 4.

The molar excess enthalpies H^E (at 293.15 K) and the molar excess isobaric heat capacities $C_p{}^E$ (at 293.15 and 313.15 K) at atmospheric pressure were measured with a dynamic flow and a differential flow microcalorimeter, respectively, of Picker type (Setaram). At equimolar composition, H^E could be measured with a relative error of less than 2.5%. The absolute molar C_p values of 2,2,4-trimethylpentane were estimated to be accurate to 1.2 J mol^{-1} K^{-1}; the errors for C_p of 2-chloro-2-methylpropane and chlorobenzene were estimated to be 1%. In a stepwise procedure, only small differences of the volumetric heat capacities were measured from one concentration to another one over the entire range, for which uncertainties in the heat capacity of the pure compounds did not matter; from this $C_p{}^E$ could be determined with an accuracy of 0.02 J mol^{-1}

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Table I. Densities ρ, Molar Isobaric Heat Capacities C_p, Vapor Pressures p, and Refractive Indexes n_D of the Pure Liquids at Temperature T

	2-chloro-2-methylpropane		chlorobenzene		2,2,4-trimethylpentane	
T/K	exptl	lit.	exptl	lit.	exptl	lit.
			ρ/(g cm^{-3})			
293.15	0.842 92	0.8420 (*11*)	1.106 53	1.1063 (*11*)	0.691 89	0.691 93 (*11*)
298.15	(0.836 67)[a]	0.8361 (*11*)			(0.687 72)[a]	0.687 81 (*11*)
313.15	0.818 23		1.084 98		0.675 37	0.675 38 (*12*)
			C_p/(J mol^{-1} K^{-1})			
293.15	161.93		148.52		237.85	
298.15			(150.70)[b]	146.02 (*13*)	(240.90)[b]	238.50 (*11*)
313.15	169.81		155.54		252.48	246.80 (*14*)
			p/kPa			
303.15			2.110	2.078 (*15*)	8.334	8.322 (*16*)
323.15			5.839	5.666 (*15*)	19.634	19.540 (*16*)
			n_D			
293.15			1.5244	1.5241 (*11*)	1.3912	1.3915 (*11*)

[a] Calculated by linear interpolation of ρ between 293.15 and 313.15 K. [b] Calculated by linear interpolation of the volumetric heat capacities between 293.15 and 313.15 K.

Table II. Index of Refraction n_D of the Liquid System Chlorobenzene (1) + 2,2,4-Trimethylpentane (2) at 293.15 K as a Function of Mole Fraction x_2

x_2	n_D	x_2	n_D	x_2	n_D
0.114 14	1.5024	0.433 77	1.4519	0.790 21	1.4098
0.197 41	1.4878	0.492 31	1.4440	0.898 27	1.4003
0.306 19	1.4700	0.687 90	1.4194		

Table III. Molar Excess Volumes V^E as a Function of Mole Fraction x_2 at Temperature T and Atmospheric Pressure

2-chloro-2-methylpropane (1) + 2,2,4-trimethylpentane (2)			chlorobenzene (1) + 2,2,4-trimethylpentane (2)		
	V^E/(cm^3 mol^{-1})			V^E/(cm^3 mol^{-1})	
x_2	T = 293.15 K	T = 313.15 K	x_2	T = 293.15 K	T = 313.15 K
0.083 77	0.134	0.149	0.029 52	−0.045	−0.053
0.188 78	0.260	0.298	0.069 41	−0.100	−0.116
0.244 23	0.331	0.375	0.129 17	−0.171	−0.197
0.276 31	0.356	0.404	0.136 11	−0.178	−0.203
0.364 74	0.407	0.468	0.232 64	−0.250	−0.292
0.489 22	0.451	0.504	0.336 08	−0.290	−0.343
0.492 95	0.454	0.513	0.528 23	−0.288	−0.335
0.514 36	0.455	0.506	0.532 77	−0.280	−0.331
0.583 71	0.444	0.496	0.711 53	−0.196	−0.239
0.597 01	0.442	0.488	0.717 13	−0.195	−0.230
0.665 56	0.411	0.451	0.775 11	−0.152	−0.187
0.672 23	0.407	0.443	0.819 25	−0.127	−0.154
0.808 31	0.282	0.308	0.820 91	−0.123	−0.155
0.915 40	0.144	0.153	0.922 43	−0.056	−0.068

Table IV. Molar Excess Enthalpies H^E as a Function of Mole Fraction x_2 at 293.15 K and Atmospheric Pressure

2-chloro-2-methylpropane (1) + 2,2,4-trimethylpentane (2)		chlorobenzene (1) + 2,2,4-trimethylpentane (2)	
x_2	H^E/(J mol^{-1})	x_2	H^E/(J mol^{-1})
0.0709	146	0.1263	339
0.1390	270	0.1608	409
0.1682	303	0.1976	486
0.1953	343	0.2457	562
0.2495	417	0.2752	595
0.3102	488	0.3023	617
0.3725	536	0.3594	652
0.3946	547	0.3813	660
0.4416	561	0.4202	667
0.5093	570	0.4844	665
0.5857	560	0.5492	646
0.6626	508	0.6317	573
0.7117	456	0.7080	486
0.8304	311	0.7957	345
0.9423	116	0.8698	225

K^{-1} at equimolar composition and 293.15 K. In both calorimeters the mole fractions x_i were accurate to 1×10^{-4}. Experimental details may be found for H^E in ref 5 and for C_p^E in ref 1.

The molar excess Gibbs energy G^E of chlorobenzene + 2,2,4-trimethylpentane was calculated from vapor pressure measurements by a conventional dynamic isothermal glass apparatus of Cottrell type (*6*), as described in the literature (*7*). The temperature T, measured by means of a mercury thermometer, was kept constant to ±0.05 K. The vapor pressure was measured by means of a mercury manometer read by a cathetometer; a manostat buffered the equilibrium pressure to 0.04 kPa. The equilibrium concentrations of the liquid phase were determined from measurements of the refractive index of small samples withdrawn from the system, which led to accuracies in the mole fractions x_i of 5×10^{-4}. The refractive indexes were measured by an Abbé refractometer (Carl-Zeiss-Jena) with a precision of 10^{-4} and are presented as a function of the mole fraction in Table II. The vapor pressures at 303.15 and 323.15K were approximated by cubic splines, with maximum deviations of, respectively, 0.087 and 0.075 kPa; the mole fractions in the vapor phase $y_{i,\mathrm{calc}}$ were calculated by integration of the Gibbs–Duhem equation (fourth-order Runge–Kutta, neglecting molar volume of the liquid and assuming ideality in the vapor phase) (*8*) and differences $\Delta y_i = y_i - y_{i,\mathrm{calc}}$ were only calculated in order to check possible systematic errors in the dynamic measurements (e.g. by insufficient condensing of the vapor phase). Finally, activity coefficients and G^E were determined from the measured p–x_2 and the calculated $y_{2,\mathrm{calc}}$ data. The accuracy of G^E was estimated to be 3%.

Results and Discussion

The molar excess volumes V^E are presented in Table III, the molar excess enthalpies H^E in Table IV, and the molar excess isobaric heat capacities C_p^E in Table V. The measured mole fractions x_2 in the liquid, y_2 in the vapor phase, the difference Δy_2 between measured and calculated y_2 values, measured vapor pressures p, and the calculated molar excess Gibbs energies G^E of the system chlorobenzene + 2,2,4-trimethylpentane are summarized in Table VI. All the excess properties have been fitted to Redlich–Kister type polynomials:

$$Z_{\mathrm{calc}}^E = x_1 x_2 [\sum_{i=0}^{k} A_i (x_1 - x_2)^i] \qquad (1)$$

where Z^E is V^E/(cm^3 mol^{-1}), H^E/(J mol^{-1}), C_p^E/(J mol^{-1} K^{-1}), or

Table V. Molar Excess Isobaric Heat Capacities C_p^E as a Function of Mole Fraction x_2 at Temperature T and Atmospheric Pressure

2-chloro-2-methylpropane (1) + 2,2,4-trimethylpentane (2)				chlorobenzene (1) + 2,2,4-trimethylpentane (2)			
T = 293.15 K		T = 313.15 K		T = 293.15 K		T = 313.15 K	
x_2	$C_p^E/(J\ mol^{-1}\ K^{-1})$	x_2	$C_p^E/(J\ mol^{-1}\ K^{-1})$	x_2	$C_p^E/(J\ mol^{-1}\ K^{-1})$	x_2	$C_p^E/(J\ mol^{-1}\ K^{-1})$
0.0205	0.030	0.0268	−0.007	0.0334	−0.086	0.0488	−0.116
0.1354	0.087	0.1438	−0.054	0.0598	−0.143	0.1409	−0.323
0.2673	0.026	0.2706	−0.117	0.1017	−0.218	0.2611	−0.518
0.3474	−0.042	0.4181	−0.185	0.1488	−0.285	0.3797	−0.632
0.4351	−0.128	0.4548	−0.211	0.2464	−0.424	0.5119	−0.717
0.5208	−0.197	0.5225	−0.249	0.3828	−0.529	0.5538	−0.724
0.5788	−0.237	0.5921	−0.275	0.4877	−0.568	0.6657	−0.666
0.6295	−0.254	0.6359	−0.262	0.6038	−0.568	0.7859	−0.546
0.7426	−0.240	0.7407	−0.269	0.7161	−0.489	0.8291	−0.478
0.8867	−0.118	0.8651	−0.180	0.8291	−0.349	0.9573	−0.140
0.9431	−0.073	0.9373	−0.099	0.9117	−0.187		

Table VI. Measured Liquid x_2 and Vapor y_2 Mole Fractions, Difference $\Delta y_2 = y_2 - y_{2,calc}$ (See Text), Vapor Pressure p, and Calculated Molar Excess Gibbs Energy G^E of the Liquid System Chlorobenzene (1) + 2,2,4-Trimethylpentane (2) at Temperature T

T = 303.15 K					T = 323.15 K				
x_2	y_2	Δy_2	p/kPa	$G^E/(J\ mol^{-1})$	x_2	y_2	Δy_2	p/kPa	$G^E/(J\ mol^{-1})$
0.0203	0.1501	0.0052	2.561	39.5	0.0102	0.0801	0.0104	6.171	21.4
0.0931	0.4330	0.0048	3.571	167.5	0.0203	0.1103	−0.0180	6.550	41.9
0.1649	0.5479	−0.0147	4.247	273.3	0.0351	0.1900	−0.0099	7.127	70.9
0.2351	0.6283	−0.0135	4.857	356.8	0.0552	0.2705	−0.0071	7.684	108.2
0.3283	0.6870	−0.0238	5.428	437.3	0.0948	0.3871	−0.0011	8.681	174.9
0.4601	0.7550	−0.0217	6.252	492.0	0.1442	0.4649	−0.0167	9.745	246.4
0.5602	0.8102	−0.0060	6.649	487.3	0.1932	0.5278	−0.0200	10.790	305.5
0.6631	0.8480	−0.0058	7.047	441.1	0.2731	0.6134	−0.0127	12.123	378.8
0.7500	0.8819	−0.0041	7.432	369.5	0.3920	0.6851	−0.0240	13.762	441.2
0.8382	0.9148	−0.0065	7.711	266.7	0.4731	0.7299	−0.0243	14.691	455.2
0.8920	0.9512	0.0062	7.936	189.2	0.6180	0.8048	−0.0183	16.324	426.9
					0.7621	0.8751	−0.0098	17.651	331.1
					0.8503	0.9150	−0.0082	18.368	236.0

Table VII. Coefficients A_i of Redlich–Kister Fits, Equation 1, to Measured Data, Standard Deviations σ, Equation 2, and Maximum Deviations δ, Equation 3, for the Liquid Systems Polar Component (1) + 2,2,4-Trimethylpentane (2) at Temperature T

polar component	excess property	T/K	A_0	A_1	A_2	σ	δ
2-chloro-2-methylpropane	V^E	293.15	1.816	0.086	−0.055	0.004	0.007
	V^E	313.15	2.034	0.004	−0.120	0.003	0.006
	H^E	293.15	2290	−9	−200	4.4	7.7
	C_p^E	293.15	−0.745	−1.450	0.933	0.007	0.014
	C_p^E	313.15	0.937	−0.823	−0.109	0.007	0.011
	G^E[a]	293.15	994	87	77	2.8	5.7
chlorobenzene	V^E	293.15	−1.162	0.476	0.021	0.003	0.005
	V^E	313.15	−1.367	0.507	−0.001	0.002	0.003
	H^E	293.15	2657	−738	−181	5.8	8.9
	C_p^E	293.15	−2.293	−0.118	−0.200	0.009	0.016
	C_p^E	313.15	−2.836	−0.519	−0.339	0.008	0.012
	G^E[b]	303.15	1980	−13	−9		
	G^E[b]	323.15	1820	−99	210		

[a] From ref 10. [b] Calculated from cubic spline fit of vapor pressures, therefore no meaningful values of σ and δ available.

$G^E/(J\ mol^{-1})$, respectively. The coefficients A_i are summarized in Table VII, together with the standard deviation σ defined as

$$\sigma^2 = \sum_N [Z^E - Z_{calc}^E]^2/(N - m) \qquad (2)$$

where N is the number of data points and m the number of coefficients A_i, and the maximum deviation δ

$$\delta = \max |Z^E - Z_{calc}^E| \qquad (3)$$

The V^E and C_p^E values can be compared with literature data (*9*). Whereas the V^E values agree within the combined limits of error, the present C_p^E values are a bit more negative and more symmetric.

As discussed previously (*1*), part of the positive G^E and H^E values are due to dipole–dipole interaction and reduced molecular mobility in the pure polar liquids, which is broken up in the process of mixing. However, in both systems this interaction is fairly weak, as the reduced dipole moments of 2-chloro-2-methylpropane and chlorobenzene are small. The excess entropy in the system 2-chloro-2-methylpentane + 2,2,4-trimethylpentane is fairly large, as can be seen when H^E values are compared to previously published G^E values (*10*). In both mixtures, C_p^E is negative over most of the, if not the entire, concentration range.

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Glossary

A_i	coefficients in eq 1
C_p	molar isobaric heat capacity, J mol^{-1} K^{-1}
G	molar Gibbs energy, J mol^{-1}
H	molar enthalpy, J mol^{-1}
n_D	refractive index
p	pressure, Pa
T	temperature, K
V	molar volume, cm^3 mol^{-1}
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
Z	any quantity Z (V, H, C_p, or G) divided by corresponding unit

Greek Letters

δ	maximum deviation in units of fitted data, eq 3
ρ	density, g cm^{-3}
σ	standard deviation in units of fitted data, eq 2

Subscript

calc	calculated value

Superscript

E	excess quantity

Registry No. Chlorobenzene, 108-90-7; 2-chloro-2-methylpropane, 507-20-0; 2,2,4-trimethylpentane, 540-84-1.

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Thermodynamic Properties of Aqueous Electrolyte Solutions. 3. Vapor Pressure of Aqueous Solutions of $LiNO_3$, $LiCl + LiNO_3$, and $LiBr + LiNO_3$†

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Vapor pressures were determined for binary and ternary mixtures of H_2O–$LiNO_3$, H_2O–$LiCl + LiNO_3$ (salt mole ratio 0.88:0.12), and H_2O–$LiBr + LiNO_3$ (salt mole ratio 0.70:0.30) at 303.15–373.15 K and in the range of concentration from 9.874 to 60.687 wt %. The vapor pressure measurements were made by the differential static method. Experimental data were fitted to the Antoine type of equation $\log (P/\mathrm{kPa}) = A(X) + B(X)/(T/\mathrm{K}^{-1}) + C(X)/(T^2/\mathrm{K}^{-2})$, where A, B, and C are concentration-dependent parameters. The calculated values from these equations were in good agreement with the experimental data.

Introduction

In continuation with our earlier work (*1–3*), precise measurements of vapor pressures of aqueous electrolyte solutions of $LiNO_3$, $LiCl + LiNO_3$, and $LiBr + LiNO_3$, over the concentration range 9.874–60.687 wt % and at temperatures between 303.15 and 373.15 K have been undertaken. The experimental vapor pressure data for the aqueous electrolyte solutions were fitted to the Antoine type of equation. These data may be useful for calculating the theoretical coefficient of performance and hence the design of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers. Iyoki and co-workers (*4*, *5*) studied the vapor pressures of aqueous solutions of $LiBr + ZnCl_2 + CaBr_2$ and $LiBr + LiI$ at 280.85–383.05 K and in the range of concentrations 10–64.5 wt %. Also they discussed the use of the above mixtures in the absorption heat pumps. A literature survey revealed that vapor pressure data are not available for these systems except a few data for aqueous $LiNO_3$ (*6*, *7*).

Experimental Section

Materials. Stock solutions were prepared from the following anhydrous analytical reagents (purity): LiCl (+99%) (Hans Heinrich-Hutte, GmbH, Germany), LiBr (+99%) (Aldrich Chemical Co.), and $LiNO_3$ (>98%) (Fluka, Switzerland).

All salts were dried in a vacuum oven at 120 °C for several days. These salts were dissolved in distilled but previously deionized water, and if necessary the solutions were filtered. The concentration of solution was changed by addition of water. The densities (ρ) were determined at 303.15 K for different concentrations (w) by the use of a densimeter from Anton Paar Co., Ltd. (DMA 60/602). The densities were reproducible to $\pm 2 \times 10^{-5}$ g cm^{-3}. The ρ–w data of each system were fitted to a polynomial:

$$w/(\mathrm{wt}\ \%) = A + B(\rho/(\mathrm{g\ cm^{-3}})) + C(\rho^2/(\mathrm{g^2\ cm^{-6}})) + D(\rho^3/(\mathrm{g^3\ cm^{-9}})) \quad (1)$$

The fitting constants A, B, C, and D along with the average percent deviations are given in Table I for all the systems at

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