

THERMODYNAMIC EXCESS PROPERTIES IN BINARY MIXTURES OF MOLECULES OF DIFFERENT SIZES AND SHAPES

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Isothermal vapour-liquid equilibrium (VLE) data for binary mixtures of 2-propanone with 1-chloropentane (I), 1,3-dichloropropane (II), 1,4-dichlorobutane (III), 1,1,1-trichloroethane (IV) and 1,1,2,2-tetrachloroethane (V), within the 298.15-313.15 K temperature range are evaluated.

Total vapour pressures were measured by a static method, the mixtures being prepared by weight and degassed directly into the working cell. The experimental data were correlated by Barker's method and different expressions for excess Gibbs energy were tested. The results indicated positive (for (I), (III), (IV) mixtures) and negative (for (II), (V) mixtures) deviations from ideality.

Our G^E and H^E values obtained from VLE data and those available in the literature are compared. These evidenced the existence of the specific interactions (H bonding) between the components of the mixtures and the proximity effects of the Cl atoms.

For 2-propanone + α,ω -dichloroalkanes, G^E and H^E (algebraic) values increase in the order: dichloromethane > 1,2-dichloroethane > 1,3-dichloropropane > 1,4-dichlorobutane. For 2-propanone + polychloroalkanes, G^E and H^E decrease in the sequence: tetrachloromethane > 1,1,1-trichloroethane > dichloroethane > trichloromethane > 1,1,2,2-tetrachloroethane. The H bond strength increases from dichloromethane to 1,1,2,2-tetrachloroethane.

Introduction

Direct measurement of the characteristic excess properties of binary non-electrolyte solutions, where the differences in molecular size, shape, volatility, and other physical properties of the components are relevant, has gained much importance in the recent years. In keeping with this trend, we present the results of our measurement of excess Gibbs energy, G^E , obtained by a static equilibrium method, for 2-propanone + 1-chloropentane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane mixtures within the temperature range 298.15K-313.15K.

Beside our G^E and H^E values determined from VLE data [1,2], the excess data available in literature on 2-propanone + other chloroalkanes mixtures, are considered, and a comparison of the thermodynamic properties of these binary systems is advanced.

Chloroalkanes and ketones have an important application both in the chemical industry, as solvents and intermediates and from a theoretical point of view, their mixtures being useful for studying the interaction between the Cl group and the CO group [3÷6].

The results on our study and on other ketones + chloroalkanes mixtures will be used for estimating interaction parameters for group contribution methods.

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Experimental

Apparatus and procedure

The vapour pressure measurements of pure compounds and binary mixtures were carried out by a static method. Use has been made of an isoteniscope built up by us upon Surovy's model [7]. The working procedure and the performance of the apparatus were described in previous papers [1,2,8].

Samples with a volume of about 10 cm^3 of known composition were prepared by weight ($\pm 0.1 \text{ mg}$) and thoroughly degassed into the equilibrium cell; the degassing procedure of alternate freezing, pumping to high vacuum and thawing, (6-8 cycles) was similar to that used by Ronc and Ratcliff [9] and Young et. al. [10].

The solutions in the equilibrium cell were stirred during the pressure measurements by the help of a magnetic stirrer and equilibrium was obtained within 1 h. After thermostating the equilibrium cell to within 0.05 K at the required temperature, the pressure exerted by the vapours is balanced with air in a null-type mercury manometer. In turn, the air pressure is measured at an external mercury manometer connected to the isoteniscope. The manometer readings were performed with a Griffin and George Ltd. (London, Gt.Britain) Type 4214 cathetometer to $\pm 0.01 \text{ mm}$, and the pressure reproducibility was estimated to be better than 20 Pa. The measured values of the vapour pressure were corrected for mercury temperature and local gravity.

The temperature of the liquid sample was measured with an accuracy of $\pm 0.05 \text{ K}$ by means of a set of Beckmann thermometers, previously checked.

The final composition of the mixtures was determined refractometrically at 298.15K, ($\sigma(x) = 0.001$ mole fraction).

Materials

Substances used were commercial products from E. Merck A G (Darmstadt and Schuchardt) of the first grade of purity, not less than 99.8 mole % GC. The liquids were dried and stored over 4A molecular sieves and used without further purification. 1,1,2,2-tetrachloroethane, purum material ($\sim 98 \%$, Fluka) was rectified on a 30-plate column packed with glass helices. After rectification it was stored in a refrigerator. Purity determined by gas chromatography was better than 99.4 %.

Evidence of purity is illustrated by comparison of measured refractive indices, $n_D^{298.15 \text{ K}}$, densities, $\rho^{298.15 \text{ K}}$ in Table 1

Table 1. Physical properties of pure compounds

Compound	$n_D^{298.15\text{K}}$		$\rho^{298.15\text{K}}$ (kg/m ³)	
	This work	Literature	This work	Literature
2-propanone	1.3579	1.3561 a	784.4	784.2 a
1-chloropentane	1.4101	1.4099 b	879.8	876.9 b
1,3-dichloropropane	1.4459	1.4460 c	1180.5	1178.2 c
1,4-dichlorobutane	1.4520	1.4522 d	1135.0	1134.2 d
1,1,1-trichloroethane	1.4350	1.4358 e	1331.3	1330.3 e
1,1,2,2-tetrachloroethane	1.4917	1.4918 f	1587.6	1586.8 f

^a[11]; ^b[12]; ^c[13]; ^d[14]; ^e[12]; ^f[14].

Data Reduction

The VLE data of the mixtures were reduced using Barker's method [15].

In this method the parameters in an expression for the excess Gibbs energy of the liquid phase are obtained by minimizing the sum of the squares between the measured and calculated pressures. ($P_{\text{exp.}} - P_{\text{calc.}}$) With this procedure a functional form is assumed for the composition dependence of the molar excess Gibbs free energy G^E . Here we chose the Redlich-Kister [16] expression

$$G^E / RT = x_1(1 - x_1) \cdot \sum_{i=1}^m A_i (1 - 2x_1)^i \quad (1)$$

The activity coefficients γ_i are obtained by differentiation of eq. (1)

$$\ln \gamma_1 = (1 - x_1)^2 \left[A_0 + \sum_{i=1}^m \left\{ A_i (1 - 2x_1)^i - 2i A_i x_1 (1 - 2x_1)^{i-1} \right\} \right] \quad (2)$$

$$\ln \gamma_2 = x_1^2 \left[A_0 + \sum_{i=1}^m \left\{ A_i (1 - 2x_1)^i - 2i A_i (1 - 2x_1)^{i-1} \right\} \right] \quad (3)$$

where x_1 denotes the mole fraction of 2-propanone in the liquid phase.

The calculated pressures are given by:

$$P_{\text{calc}} = x_1 \gamma_1 p_1^0 D_1 + x_2 \gamma_2 p_2^0 D_2 \quad (4)$$

using for non-ideality of the vapour phase the corrections:

$$D_1 = \exp \left[\left\{ (V_1^0 - B_{11})(P - p_1^0) - P \delta_{12} y_2^2 \right\} / RT \right] \quad (5)$$

$$D_2 = \exp \left[\left\{ (V_2^0 - B_{22})(P - p_2^0) - P \delta_{12} y_1^2 \right\} / RT \right] \quad (6)$$

where V_1^0 and V_2^0 are the molar volumes, p_1^0 and p_2^0 are the vapour pressures of pure components, y_1 and y_2 are the vapour phase mole fractions, and δ_{12} is given by:

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (7)$$

with B_{11} , B_{22} , the second virial coefficients of pure compounds and B_{12} , the cross second virial coefficient.

Vapour phase correction was estimated by the two-terms virial equation whose second virial coefficients for pure compounds and for mixture were calculated according to Tsonopoulos [17]. The molar volumes were obtained using Rackett's equation.

Critical properties of substances were taken from Ambrose's report [18].

Results

The experimental vapour pressures data of the binary mixtures are presented in the Figs. 1–5. These figures show the experimental and calculated isotherms fitted with 3rd order Redlich-Kister equation; a very good agreement between data is observed.

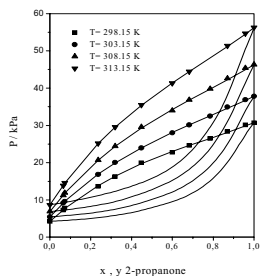


Fig.1: VLE data for 2-propanone + 1-chloropentane

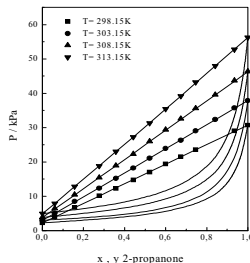


Fig.2: VLE data for 2-propanone + 1,3-dichloropropane

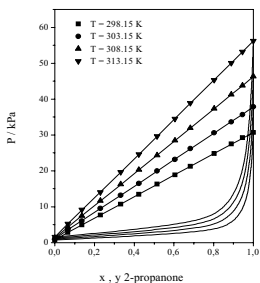


Fig.3: VLE data for 2-propanone + 1,4-dichlorobutane

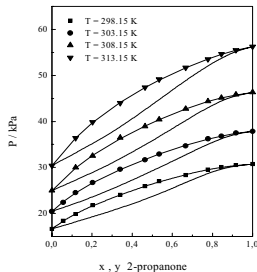


Fig. 4: VLE data for 2-propanone + 1,1,1-trichloroethane

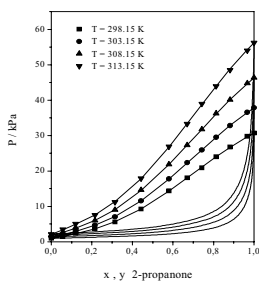


Fig. 5: VLE data for 2-propanone + 1,1,2,2-tetrachloroethane

Tables 2 and 3 present, for exemplification, the experimental data and the calculated ones: mole fraction of vapour phase, y , the activity coefficients, γ_1 and γ_2 and the G^E values,

fitted by means of Redlich-Kister equation at $T=313.15$ K, in the case of 2-propanone + 1,4-dichlorobutane and 2-propanone + 1,1,2,2-tetrachloroethane mixtures.

Table 2. Experimental and calculated VLE data in 2-propanone +1,4-dichlorobutane binary mixture at $T = 313.15$ K.

x_1	y_1 calc	P_{exp} (kPa)	P_{calc} (kPa)	$P_e - P_c$ (kPa)	γ_1	γ_2	G^E (J/ mol)
0.000	0.000	1.60	1.60	0.00	1.0263	1.0000	0
0.065	0.708	5.24	5.16	0.08	1.0258	1.0000	4
0.136	0.845	9.13	9.03	0.10	1.0246	1.0002	9
0.229	0.911	14.05	14.08	-0.03	1.0223	1.0007	14
0.332	0.944	19.66	19.69	-0.03	1.0190	1.0020	20
0.424	0.961	24.53	24.66	-0.07	1.0156	1.0040	23
0.515	0.972	29.64	29.62	0.02	1.0121	1.0071	25
0.605	0.980	34.51	34.54	-0.03	1.0087	1.0115	25
0.683	0.986	38.90	38.75	0.15	1.0060	1.0164	24
0.802	0.992	45.32	45.25	0.07	1.0026	1.0266	19
0.889	0.996	50.03	50.02	0.01	1.0009	1.0362	12
0.945	0.998	53.21	53.14	0.07	1.0002	1.0435	7
1.000	1.000	56.23	56.23	0.00	1.0000	1.0517	0

Table 3. Experimental and calculated VLE data in 2-propanone + 1,1,2,2-tetrachloroethane binary mixture at $T = 313.15$ K.

x_1	y_1 calc	P_{exp} (kPa)	P_{calc} (kPa)	$P_e - P_c$ (kPa)	γ_1	γ_2	G^E (J/ mol)
0.000	0.000	2.13	2.13	0.00	0.4415	1.0000	0
0.056	0.403	3.45	3.37	0.08	0.4479	0.9995	-118
0.120	0.619	5.08	4.92	0.16	0.4668	0.9953	-249
0.214	0.785	7.55	7.64	-0.09	0.5134	0.9760	-422
0.314	0.878	11.22	11.35	-0.13	0.6821	0.9326	-567
0.443	0.943	17.87	17.83	0.04	0.6916	0.8388	-680
0.581	0.975	26.83	26.74	0.09	0.8142	0.7064	-690
0.670	0.986	33.23	33.32	-0.09	0.8852	0.6144	-631
0.742	0.992	38.93	38.75	0.18	0.9316	0.5435	-546
0.812	0.995	43.94	43.95	-0.01	0.9656	0.4797	-433
0.882	0.998	48.47	48.84	-0.37	0.9875	0.4240	-292
0.966	0.999	53.99	54.24	-0.25	0.9991	0.3687	-90
1.000	1.000	56.23	56.23	0.00	1.0000	0.3506	0

The parameters of the equation (1) used in correlation and the values of standard deviation $\sigma(P)$ are listed in Table 4.

Table 4. Parameters of the Redlich-Kister equation used to correlate VLE data for 2-propanone + chloroalkanes mixtures and standard deviation $\sigma(P)$ at 298.15 / 303.15 / 308.15 / 313.15 K

Redlich-Kister equation		Parameters and $\sigma(P)$ / kPa			
2-propanone + 1-chloropentane					
m = 3	A ₁	0.65432	0.62307	0.60277	0.57830
	A ₂	0.09864	0.06627	0.06847	0.04546
	A ₃	0.05881	0.05530	0.02862	0.01009
		0.18	0.14	0.23	0.11
2-propanone + 1,3-dichloropropane					
m = 3	A ₁	-0.01478	-0.02536	-0.02506	-0.04288
	A ₂	-0.02070	-0.02715	-0.01701	-0.03052
	A ₃	0.06014	0.04778	0.04114	-0.00062
		0.08	0.10	0.08	0.07
2-propanone + 1,4-dichlorobutane					
m = 3	A ₁	0.0657	0.0473	0.0405	0.0424
	A ₂	-0.0124	-0.0111	-0.0007	0.0016
	A ₃	0.0514	0.0445	0.0233	0.0312
		0.11	0.10	0.07	0.08
2-propanone + 1,1,1-trichloroethane					
m = 3	A ₁	0.42694	0.41475	0.42934	0.42969
	A ₂	0.01989	0.01010	0.01353	-0.01336
	A ₃	0.11801	0.09241	0.07542	0.04912
		0.06	0.09	0.09	0.07
2-propanone + 1,1,2,2-tetrachloroethane					
m = 3	A ₁	-1.2570	-1.2661	-1.1775	-1.0736
	A ₂	-0.00651	-0.0301	-0.0648	-0.1152
	A ₃	0.1371	0.1113	0.1013	0.1408
		0.10	0.06	0.09	0.18

$\sigma(P)$ is the average standard deviation of the total vapour pressure:

$$\sigma(P) = \left[\frac{\sum (P_{\text{exp}} - P_{\text{calc}})^2}{(N - m)} \right]^{1/2}, \text{ where: } N = \text{nr of experimental points; } m = \text{nr of equation parameters.}$$

Discussions

The presented results show positive deviations from the Raoult's law for (I), (III), (IV) mixtures and negative deviations, for (II), (V) mixtures.

The calculated molar excess Gibbs energies G^E throughout the whole range of composition and the values taken from the literature are presented in Figs. 6 and 8 for the mixtures whose chloroalkanes were selected in two groups: (α,ω)-dichloroalkane and

polychloroalkane, respectively. As for H^E data, they are rather scarce. For the systems where these data are missing, we estimated H^E , from the temperature dependence of G^E by Gibbs-Helmholtz equation.

If in the 2-propanone + 1-chloroalkane mixtures the excess properties are positive and increase with the chloroalkane length [19], the behaviour of the 2-propanone + α,ω -dichloroalkane mixtures depend on the distance apart of the two chloro-groups [20-22]. This behaviour agrees with that expected from the proximity effect: the more the two Cl groups are separated, the more independent they become and the systems approaches those with 1-chloroalkane whose G^E and H^E are positive.

For 2-propanone + α,ω -dichloroalkanes, G^E and H^E (algebraic) values increase in the order: dichloromethane > 1,2-dichloroethane > 1,3-dichloropropane > 1,4-dichlorobutane (Figs. 6 and 7). In the case of 2-propanone + polychloroalkanes mixtures, G^E and H^E values decrease in the sequence: tetrachloromethane > 1,1,1-trichloroethane > dichloroethane > trichloromethane > 1,1,2,2-tetrachloroethane (Figs. 8 and 9).

The great negative values of G^E and H^E denote existence of specific interactions in such systems, probably owing to the hydrogen bonding between CH_2 or CH groups from chloroalkanes and oxygen of 2-propanone. The H bond strength increases from dichloromethane to 1,1,2,2-tetrachloroethane.

The same behaviour was observed in ester + dichloroalkane mixtures [3].

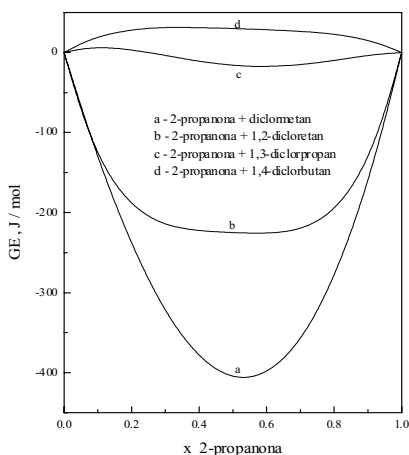


Fig. 6: G^E for 2-propanone + α,ω -dichloroalkanes mixtures
 a-T=303.15 K (CRC., 1994)
 b-T=273.15 K (Nath, 1990)
 c-T=303.15 K (our data)
 d-T=303.15 K (our data)

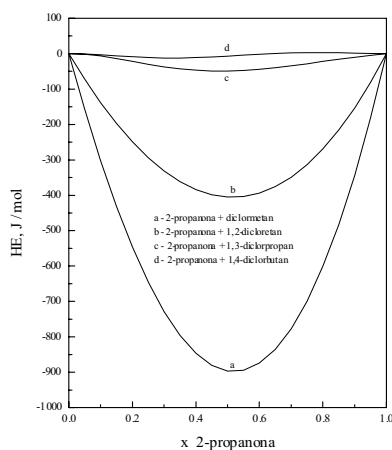


Fig. 7: H^E for 2-propanone + α,ω -dichloroalkane mixtures
 a-T=303.15 K (CRC., 1994)
 b-T=2985 K (Kechawaraz, 1990)
 c-T=298 K (Lopez, 1993)
 d-T=298 K (Lopez, 1993)

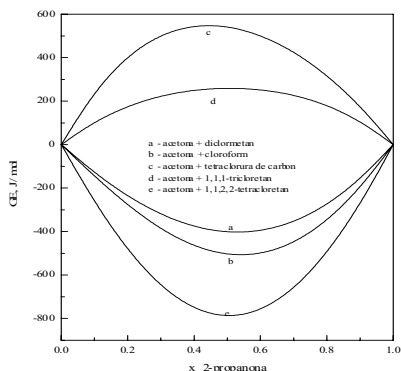


Fig. 8. G^E for 2-propanone + polychloroalkane mixtures:
 a-T=303.15 K (CRC.,1994)
 b-T=323.15 K (CRC.,1994)
 c-T=318.15K (CRC.,1994)
 d-T=303.15 K (our data)

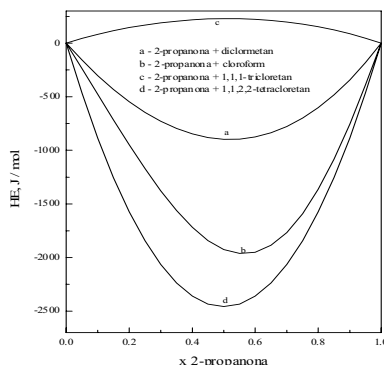


Fig.9. H^E for 2-propanone + polychloroalkane mixtures:
 a-T=303.15 K (CRC.,1994)
 b-T=2985 K (CRC.,1994)
 c-T=363.15 K (Gmehling,1992)
 d-T=305.15 K (from our VLE data)
 e-T=303.15 K(from our VLE data)

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