EXCESS THERMODYNAMIC FUNCTIONS
IN THE CARBON DISULPHIDE–CYCLOHEXANE SYSTEM

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The vapour–liquid equilibrium and the volume of mixing were measured in the carbon disulphide (1)–cyclohexane (2) system at 298·15 K. The excess functions were correlated by the Redlich–Kister expansion; smoothed values of ΔG^E, ΔV^E and ΔH^E (from orientation calorimetric measurements) were compared with results of computations by a simple perturbation theory of solutions of convex molecules.

Experimental measurements of the excess thermodynamic functions in the carbon disulphide–cyclohexane system constitute a part of our program of systematic study of equilibrium behaviour of model systems consisting of convex molecules to which may be ascribed in a simple manner convex cores corresponding to the Kihara model[1] of intermolecular interactions. Since existing equilibrium data[2-5] are inconsistent and of insufficient accuracy, we decided to perform new measurements.

EXPERIMENTAL

Pure substances. Carbon disulphide (A. R. grade, Laborchemie, Apolda) was shaken subsequently with aqueous $KMnO_4$, water, mercury and finally with saturated solution of $HgSO_4$. After washing with water and drying it was rectified to n_D^{15} 1·63182 (1·6319 (ref.[6])), d_4^{20} 1·26315 (1·2632 (ref.[6])), $t_{n.b.p.}$ 46·21° (46·25° (ref.[7])). Cyclohexane (A.R. grade, Reanal) was shaken with H_2SO_4, 5% NaOH, water, dried with $MgSO_4$ and rectified to n_D^{20} 1·4262 (1·42621 (ref.[6])), d_4^{20} 0·77853 (0·77855 (ref.[7])), $t_{n.b.p.}$ 80·70° (80·70° (ref.[6])).

Technique. The arrangement described in ref.[8] for measurements of vapour–liquid equilibria by a modified Gillespie still was used without any change; equilibrium concentrations in both phases were being determined from the dependence of the refractive index at 20°C on the mole fraction of CS_2; this dependence was expressed through the relation

$$n_D^{20} = 1·62770x_1 + 1·42625(1 - x_1) + x_1(1 - x_1) .$$
$$. \left[-0·13774 - 0·04672(2x_1 - 1) - 0·01692(2x_1 - 1)^2 \right] . \qquad (1)$$

The accuracy of our measurements was 0·0005 in composition and 0·1 Torr in pressure. For measurements of the volume of mixing, a modified dilatometer[9] was employed which enables to determine the volume of mixing within ~2% error in the vicinity of its maximum.

RESULTS AND DISCUSSION

Results of our measurements of the vapour–liquid equilibrium are summarized in Table I whose first three columns contain subsequently equilibrium compositions and pressure in the CS_2–C_6H_{12} system at 298·15 K, folloved by smoothed values of the excess Gibbs free energy and deviations in the vapour phase composition, pressure, and excess Gibbs free energy (from data correlated by the Redlich–Kister expansion and experiment). Table II contains a summarization of measured volumes of mixing at 298·15 K and deviations between correlated and experimental values of ΔV^E. The dependence of ΔG^E and ΔV^E on composition at 298·15 K is given by the equations

$$\Delta G^E/RT = x_1(1 - x_1)\left[0.3407 + 0.0830(2x_1 - 1) + 0.0289(2x_1 - 1)^2\right], \quad (2)$$

$$\Delta V^E = x_1(1 - x_1)\left[2.0589 + 0.0194(2x_1 - 1) + 0.1894(2x_1 - 1)^2\right]. \quad (3)$$

The standard deviation is 2·9 J/mol for the excess Gibbs free energy and 0·0007 cm³/mol for the excess volume. An orientation measurement of the heat of mixing on a commercial calorimeter of the Calvet type $\left(\Delta H^E = 442 \text{ J/mol at } x_1 = 0.502\right)$ gave an estimate for the enthalpy of mixing of the equimolar mixture, $\Delta H^E_{0.5} = 442$ J/mol; the approximate error of this measurement is 2%.

TABLE I

Vapour–Liquid Equilibrium in the CS_2–C_6H_{12} System at 298·15 K

x	y	P Torr	ΔG^E J/mol	Deviations		
				y	P	ΔG^E
0·0000	0·0000	97·58	0·00	----	—	—
0·0730	0·2669	123·88	48·80	0·0027	1·59	2·06
0·1228	0·3874	140·90	78·66	0·0035	1·78	2·42
0·2610	0·5992	185·22	147·10	0·0041	1·59	−3·18
0·3550	0·6910	213·08	181·12	0·0027	1·07	−2·92
0·4576	0·7647	240·65	205·45	0·0018	1·04	2·86
0·5727	0·8279	269·52	214·40	0·0010	0·41	3·52
0·6530	0·8622	287·75	207·18	0·0027	0·39	−1·94
0·7421	0·8985	307·46	183·95	0·0021	−0·27	−1·94
0·8442	0·9359	327·82	134·20	0·0029	0·20	1·22
0·8944	0·9566	339·27	99·32	0·0010	−1·20	−0·44
1·0000	1·0000	361·37	0·00	—	—	—

Excess Volumes in the CS_2–C_6H_{12} System at 298·15 K

x	ΔV^E cm³/mol	Deviation ΔV^E	x	ΔV^E cm³/mol	Deviation ΔV^E
0·0174	0·0379	0·0000	0·6190	0·4891	0·0001
0·1118	0·2137	0·0006	0·6602	0·4671	0·0005
0·2114	0·3519	0·0000	0·6886	0·4477	0·0011
0·2949	0·4328	0·0003	0·7025	0·4371	0·0013
0·3951	0·4936	−0·0005	0·8398	0·2917	−0·0012
0·4928	0·5150	−0·0004	0·8911	0·2131	−0·0006
0·5232	0·5146	−0·0006	0·9274	0·1496	−0·0005
0·5535	0·5102	−0·0003	0·9645	0·0767	0·0000
0·5816	0·5033	−0·0003	0·9948	0·0116	0·0001

Smoothed data of the excess thermodynamic functions were compared with values of ΔG^E, ΔH^E, and ΔV^E in the CS_2–cyclohexane system at 298·15 K computed by a simple perturbation theory of convex molecules[10]. We employed the expansion to first order and a special type of the "core-square-well" potential with an extremely
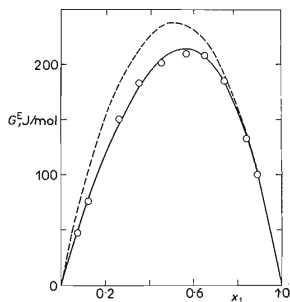

FIG. 1

The Composition Dependence of the Excess Gibbs Free Energy

The points denote experimental values, the solid line is the smoothed curve and the dashed line is the theoretical dependence.
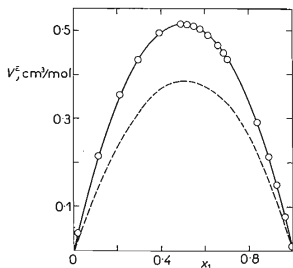

FIG. 2

The Composition Dependence of the Excess Volume

The points denote experimental values, the solid line is the smoothed curve and the dashed line is the theoretical dependence.

narrow well; parameters in this potential are determined from the heat of vaporization and the liquid density at the given temperature. The hard core of the CS_2 molecule was approximated by a rod connecting centres of both sulphur atoms. The Kihara model[11] of truncated double-cone was employed for the cyclohexane core. The cores were described by the following geometric functionals: $CS_2 - R_c = 0.776$ Å, $S_c = 0.0$ Å^2, $V_c = 0.0$ Å^3, $\xi = 1.61$ Å; cyclohexane $- R_c = 1.678$ Å, $S_c = 32.940$ Å^2, $V_c = 14.661$ Å^3, $\xi = 1.23$ Å; energetical parameters $a_{11} = 1.508$ Å, $a_{22} = 1.381$ Å, $a_{12} = (a_{11}a_{22})^{0.5}$.

The following values of the excess functions were found for the equimolar mixture: $\Delta V^E = 0.387$ cm^3/mol (expt. 0.514 cm^3/mol), $\Delta H^E = 422.5$ J/mol (expt. 442 J/mol) and $\Delta G^E = 239.2$ J/mol (expt. 211.1 J/mol). The comparison of theoretical and experimental concentration dependences of ΔG^E and ΔV^E on Figs 1, 2 and, similarly, the comparison of the excess functions of the equimolar solution point to good agreement between the theory and experiment.

This good agreement confirms the fundamental correctness of the description of repulsive forces acting among molecules of the given system through convex models as well as the possibility of using the simple perturbation theory for a practically applicable description of systems containing nonpolar nonspherical molecules.

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