Table 1 Column parameters

Polymer	Coating solvent	Loading	Polymer mass (g)	Length (cm)	O.d. (in)
Poly(ethylene oxide)	Chloroform	2.82	0.2886	100	0.25
Poly(ethylene oxide)	Chloroform	6.04	0.7840	100	0.25

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \frac{2\delta_2}{RT}\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S}{V_1}\right) \tag{7}$$

A plot of $\delta_1^2/RT - \chi/V_1$ vs. δ_1 allows us to calculate δ_2 from the slope and, replacing this value in the intercept, to estimate the entropic component χ_S.

As we will show later, both δ_i and χ_S are parameters linearly dependent on the temperature in the whole range considered. Therefore, we can extrapolate at 25°C to obtain the value of the interaction parameter at this temperature, using equation (6).

According to the equation-of-state theory[8], the residual partial molar free energy, given by $RT\chi\varphi_2^2$ in the FH theory, can be expressed by means of the following equation:

$$(\mu_1 - \mu_1^\circ)^R = P_1^* V_1^* \left[3\tilde{T}_1\ln\left(\frac{v_1^{1/3} - 1}{\tilde{v}^{1/3} - 1}\right) + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\right] + \frac{V_1^* X_{12}\theta_2^2}{\tilde{v}} \tag{8}$$

where P_1^* and V_1^* are the characteristic pressure and molar volume of the solvent, $\tilde{T}_1$ and $\tilde{v}_1$ are the reduced temperature and volume of the solvent, $\tilde{v}$ is the reduced volume of the mixture and X_{12} is the specific interaction energy. θ_2 or the site fraction is defined by the expression:

$$\theta_2 = s_2 x N_2 / (s_1 N_1 + s_2 x N_2) \tag{9}$$

where N_i are the number of molecules, x the number of segments of the polymer having the same volume as the solvent molecule and s_1 and s_2 the number of contact sites in the solvent molecule and polymer segment respectively.

In inverse gas chromatography $\theta_2 = 1$ at infinite dilution, and the reduced volume of the mixture matches with that of the polymer.

Equation (8) allows us to obtain the specific interaction energy X_{12} at the desired temperature, if the residual partial molar free energy can be determined chromatographically.

In the equation-of-state theory, the residual partial molar free energy can be rewritten as:

$$(\mu_1 - \mu_1^\circ)^R = RT\chi^*\phi_2^2 \tag{10}$$

where the only difference is that φ_2 is now calculated using characteristic specific volumes of both components, providing a χ^* value slightly different from χ.

EXPERIMENTAL

Materials

Solutes were reagent grade and were used without

further purification. The following solutes of very different characteristics were used: n-hexane, n-octane, acetone, ethyl acetate, methanol, ethanol, n-propanol, chlorobenzene, cyclohexane, benzene, toluene and diethylene glycol diethyl ether. Effort was made to use solvents and non-solvents of both polar and non-polar nature, to extend the validity of the method to more types of solutes.

The samples of poly(ethylene oxide) were obtained from Polysciences Inc., Warrington, USA ($M_w = 300\,000$).

Columns

The polymers were first dissolved in a suitable solvent (chloroform) and deposited into an inert chromatographic support by slow evaporation of the solvent with gentle stirring and heating. After vacuum drying for ~ 48 h with slight heating, the chromatographic support was packed, with the aid of a mechanical vibrator, into 0.25 in outside diameter stainless-steel columns. The weight and percentage of the stationary phase were determined by direct weighing. Column parameters are described in Table 1.

Instrumentation

Measurements were carried out on a Perkin-Elmer 3920 B gas chromatograph, equipped with a dual flame ionization detector. Nitrogen was used as the carrier gas. Methane, as a non-interacting marker, was used to correct the dead volume in the column, and the retention time was directly measured with a chronometer between the highest points of the peak of the methane and the solute. A minimum of four measurements was made for every molecular probe and for each temperature in both columns. Pressures at inlet and outlet of the column read from a mercury manometer (<0.05 mm Hg) were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a soap bubble flow meter. Three distinct gas flows, between 20 and 60 ml min^{-1} at 70°C, were used to verify the non-variation of the volume retention with the flow.

Throughout the experiment the flow rate was fixed at 30 ml min^{-1}. The oven was modified to accommodate a water bath to 90°C and an oil bath to 140°C. The bath temperature was controlled within ± 0.1°C up to 90°C and with a precision of ± 0.5°C for the oil bath.

The solute molecules, including a small amount of methane marker, were injected manually with a 10 μl Hamilton syringe (<0.01 μl).

To check the precision of the retention data from the Perkin-Elmer 3920 B gas chromatograph, specific retention volumes for benzene and toluene were compared with literature values.

DATA REDUCTION

Specific retention volumes were calculated using[9]:

$$V_g = (t_r F / w_l) J_2^3 (P_o - P_w) / 760 \tag{11}$$

where t_r is the net retention time, F is the carrier gas flow rate at 273.16K, w_l is the mass of polymer in the column, P_w is the water vapour pressure at room temperature and J_2^3 a correction factor for pressure in the column:

$$J_2^3 = \frac{3(P_i/P_o)^2 - 1}{2(P_i/P_o)^3 - 1} \tag{12}$$

where P_i and P_o are the inlet and outlet pressures. Solute vapour pressures were calculated using the Antoine equation:

$$\log P_1^\circ = A - B/(t + C) \tag{13}$$

where P_1° is the solute vapour pressure in mm Hg, t is the temperature (°C) and A, B and C are constants taken from standard sources[10], and also obtained from elsewhere[11,12].

Solute densities were obtained from Timmermans' compilation[11]. Second virial coefficients (B_{11}) were computed from ref. 13:

$$\frac{B_{11}}{V_c} = 0.430 - 0.886\left(\frac{T_c}{T}\right) - 0.694\left(\frac{T_c}{T}\right)^2$$
$$- 0.0375(n-1)\left(\frac{T_c}{T}\right)^{4.5} \tag{14}$$

and from Kreglewski's equations[14]. T_c and V_c are critical temperature and volume, T is the temperature (K) and n is a constant indicative of the number of carbon atoms in the molecule.

Flory–Huggins χ parameters were calculated using:

$$\chi = \ln\left(\frac{273.16 R v_2}{P_1^\circ V_g V_1}\right) - 1 - \frac{(B_{11} - V_1)P_1^\circ}{RT} \tag{15}$$

where v_2 represents the specific volume of the polymer which is known from the literature[15]. Weight fraction activity coefficients at infinite dilution $(a_1/w_1)^\infty$ were calculated from the equation:

$$\ln(a_1/w_1) = \chi - \ln(v_2/v_1) + 1 \tag{16}$$

which is valid for large molecular weight polymers as $\varphi_2 \to 1$.

State-equation χ^* parameters were calculated using:

$$\chi^* = \ln\left(\frac{273.16 R v_2^*}{P_1^\circ V_g V_1^*}\right) - 1 - \frac{(B_{11} - V_1)P_1^\circ}{RT} \tag{17}$$

where v_2^* is the characteristic specific volume of the

polymer and V_1^* the characteristic molar volume of the probe.

From equations (17), (10) and (8) the state-equation contact energy parameter X_{12} can be obtained from the following expression:

$$\frac{V_1^* X_{12}}{\tilde{v}_2} = RT\chi^* - P_1^* V_1^*\left[3\tilde{T}_1\ln\left(\frac{(\tilde{v}_1^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)}\right) + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\right] \tag{18}$$

where P_1^* has been calculated from the literature[16].

RESULTS AND DISCUSSION

The experimental retention volumes, activity coefficients (weight fractions), χ and χ^* parameters for 12 solutes between 70° and 140°C were computed.

Retention volumes were obtained for at least eight temperatures over each temperature range of 20°C. The specific interaction energy X_{12} has been obtained for n-hexane, n-octane, cyclohexane, benzene, toluene and chlorobenzene in the same range of temperature.

In *Table 2*, values of the second virial coefficients of different solutes, at 70°, 100° and 130°C, are given, which are used for correcting for solute non-ideality in the vapour phase. In the same table, values of solute molar volumes, obtained from densities, are also given, at the same temperatures.

The partial molar heat of mixing $\overline{\Delta H_1^\infty}$ of the solute at infinite dilution in the polymer is given by:

$$\overline{\Delta H_1^\infty} = R\frac{\partial \ln(a_1/w_1)^\infty}{\partial(1/T)} \tag{19}$$

Therefore, $\overline{\Delta H_1^\infty}$ was obtained from the slope of the best straight line through a plot of the logarithm of the activity coefficient vs. the reciprocal of the absolute temperature, as determined by a linear least-squares analysis.

The corresponding heats of solution were determined in a similar manner from:

$$\Delta H_s = -R\frac{\partial(\ln V_g)}{\partial(1/T)} \tag{20}$$

The molar enthalpies of vaporization calculated from the relationship:

$$\overline{\Delta H_v^\infty} = \overline{\Delta H_1^\infty} - \Delta H_s \tag{21}$$

Table 2 Second virial coefficients and molar volumes of probes

	$-B_{11}$ (cm³ mol⁻¹)			V_1 (cm³ mol⁻¹)		
	70	100	130	70	100	130
n-Hexane	1288	1036	853.5	140.5	148.7	157.8
n-Octane	2697	2102	1687	172.7	180.1	188.1
Methanol	1200	950.6	779.7	43.09	44.82	46.69
Ethanol	2189	1658	1313	61.73	64.72	68.02
n-Propanol	3667	2666	2043	78.66	82.13	85.91
Acetone	937.6	762.5	635.8	79.17	83.04	87.30
Ethyl acetate	1602	1263	1028	105.1	110.7	117.1
Chlorobenzene	1819	1439	1171	106.8	110.5	114.3
Benxene	1021	830.6	691.6	94.70	98.59	102.8
DEGDEE	6071	4492	3438	188.6	195.0	201.8
Toluene	1698	1337	1087	112.3	116.3	120.6
Cyclohexane	1166	950.1	792.0	115.3	120.0	125.1

Table 3 Dependence of the solubility parameter δ_1 on temperature

Solute	Slope x 10^2	Correlation, c	Intercept	δ_1 (25°C)	δ_1^a
n-Hexane	−1.230	0.9970	7.543	7.24	7.24
n-Octane	−1.168	0.9998	7.862	7.57	7.55
Cyclohexane	−1.223	0.9962	8.450	8.14	8.18
Benzene	−1.424	0.9998	9.526	9.17	9.15
Toluene	−1.194	0.9990	9.182	8.88	8.91
Chlorobenzene	−1.182	0.9989	9.816	9.52	9.51
Methanol	−2.902	0.9970	15.65	14.9	14.5
Ethanol	−2.928	0.9893	14.02	13.3	12.7
n-Propanol	−2.781	0.9970	13.14	12.5	11.9
Acetone	−2.082	0.9920	10.49	9.98	9.71
Ethyl acetate	−1.868	0.9990	9.627	9.16	9.04
DEGDEE	−1.386	0.9995	9.372	9.03	−

^{a} Bibliographic values
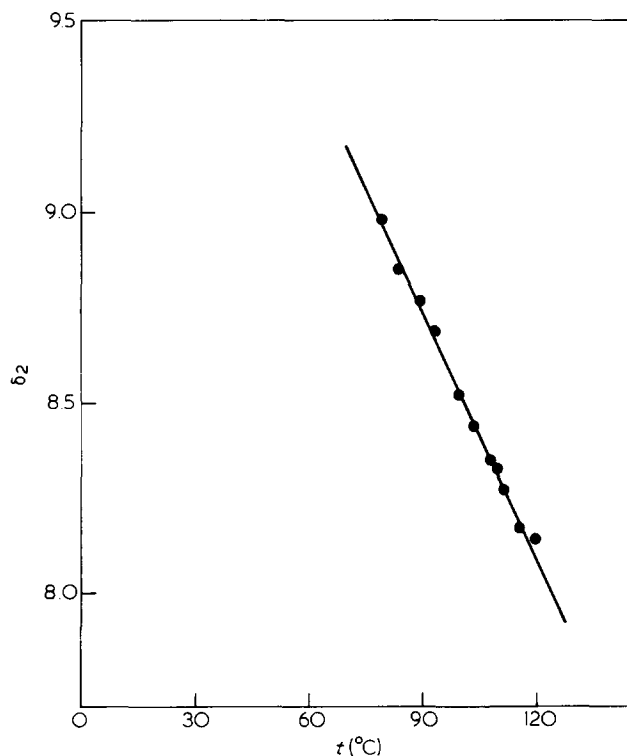
Figure 1 Variation of polymer solubility parameter δ_2 with temperature (°C)

Figure 2 Variation of the entropic contribution χ_S with temperature (°C) from equation (7) in the investigated range: (●) n-octane, (○) n-hexane, (▲) benzene and (△) ethanol

do not depend on the retention data, contrary to the observation of Ito and Guillet[17], as can be shown by a simple analysis.

The solubility parameters (δ_1) for the different solutes were calculated from the relation:

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{1/2} \qquad (22)$$

where R is the gas constant and V_1 is the solute molar volume corresponding to temperature T (K).

In *Table 3* the intercept and slope of the linear dependence of δ_1 on t (°C) are given, along with the correlation coefficient and the value at 25°C obtained by linear extrapolation from the temperature range of 70°–140°C. The values from the literature at 25°C are given for comparison. As can be shown the agreement is excellent.

Since the heat of vaporization decreases and the molar volume increases with increasing temperature, the solubility parameters of compounds decrease with increasing temperature.
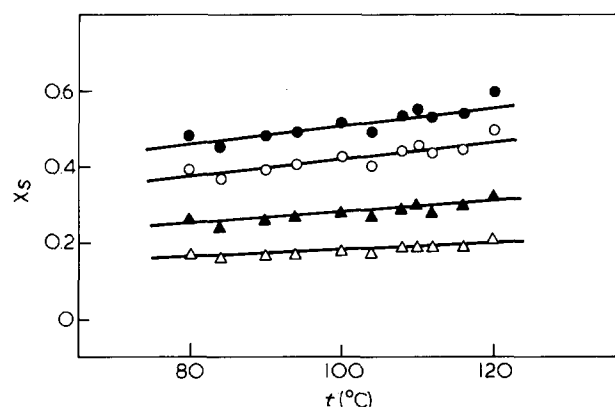
Values of the solubility parameter of the polymer, δ_2, were calculated using equation (7) for each experimental temperature. The variation of δ_2 with temperature is shown in *Figure 1*, where it can be seen that the agreement is very good and that the δ_2 value obtained by extrapolating these values (10.2) agrees satisfactorily with that obtained by the Small's group contribution method[18].

Obtaining the polymer solubility parameter by the proposed method is more applicable than that given in previous publications[6,17] for two main reasons: this method provides us with a unique value of the solubility parameter, independently of the temperature range and, on the other hand, it is not dependent on the interaction parameter χ obtained by a doubtful extrapolation method.

Apart from permitting evaluation of δ_2, equation (7) allows us to calculate the entropic contributions χ_S at various temperatures. In *Figure 2* a plot of χ_S vs. temperature is represented over the whole range investigated. The good linearity obtained enables us to extrapolate to lower temperatures.

Using equation (6) and the χ_S data mentioned above, values of the interaction parameter between 25° and 120°C were obtained.

Figure 3 shows these values of χ vs. $1/T$ as well as the experimental values obtained in the 70°–120°C range. In this figure, there is a deviation between the values calculated from equation (6) and the experimental ones. This deviation can be explained on the basis of the
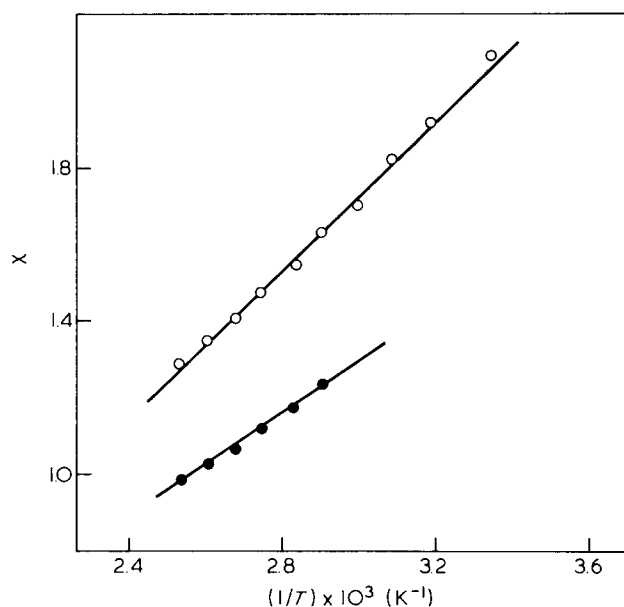
Figure 3 Variation of interaction parameter χ with reciprocal temperature (K): (●) experimental values in the range 70—120°C and (○) values from equation (6) between 25° and 120°C for the PEO/n-hexane system

dependence of the fraction χ_S/V_1 on δ_1 as has been discussed by Lipson and Guillet[19].

In this work, we intend to demonstrate that χ_s, besides being different for each polymer/solute system, is also a linear function of temperature. This behaviour, contrary to the generalized idea of a constant value for χ_S (0.3) for all systems, is closer to the physical meaning of this entropic contribution. For calculating χ_S in a more reliable way, we have employed equation (6), using the experimental values of χ, δ_1 and δ_2. *Figures 4* and *5* show plots of χ_S against t (°C) for all the systems investigated in the temperature range 70°–130°C. Except for methanol, ethanol and n-propanol, where little variations were found and we have adopted an average value, there is a linear dependence of χ_S with temperature which will allow us to obtain values of the entropic contribution at any desired temperature.

In order to compare our data with those obtained by other authors, the only ones encountered in the literature for PEO are the systems PEO/benzene[15], where extrapolation of the experimental data at $\varphi_2 = 1$ provides a χ value of 0.20 at 57.9°C, and PEO/toluene[20] at 42°C, where by extrapolation of data up to $\varphi_2 = 0.5$, we have obtained at $\varphi_2 = 1$ a χ value of 0.50. However, we must take into account that this result can be affected by a large error due to the inherent difficulties in extrapolating from 0.5 to 1. Using equation (6) we have obtained values of χ at 42°C in toluene and 57.9°C in benzene which are 0.40 and 0.24 respectively, in fair agreement with those obtained by other techniques[15,20].

The interaction parameter χ^* of the equation-of-state theory has been computed by equation (17). *Figures 6* and *7* show this parameter against the reciprocal of the temperature. As can be observed, the behaviour is similar to that of χ of the FH theory, with a minimum for the following systems: PEO/ethyl acetate, PEO/toluene, PEO/benzene and PEO/acetone. For the other systems, in the temperature range investigated, such minima do not appear, but there is some evidence of their existence, either at higher temperatures, as is the case of PEO with

diethylene glycol diethyl ether, cyclohexane, n-hexane, methanol, ethanol and n-propanol, or at lower temperatures (PEO with chlorobenzene and n-octane). The minimum depends on the investigated mixture and indicates the temperature of the highest solubility of the pair.

The more representative parameter for measuring, specifically, the interaction energy between the components of the mixture is the specific contact or interaction energy X_{12}. This parameter of the equation-of-state theory has been computed from equation (18), in
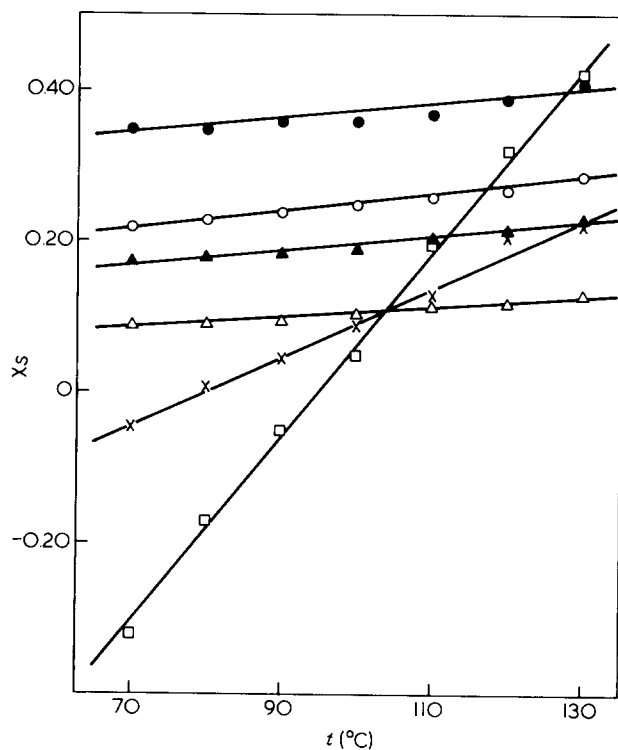

Figure 4 Variation of the entropic contribution χ_S with temperature (°C) from equation (6), for the following solutes: (●) ethyl acetate, (○) toluene, (▲) benzene, (x) n-hexane, (△) chlorobenzene and (□) n-octane
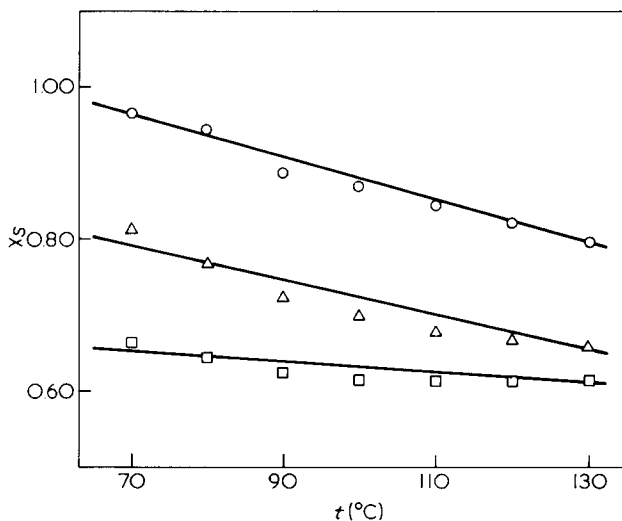

Figure 5 Variation of the entropic contribution χ_S with temperature (°C) from equation (6), for the following solutes: (○) cyclohexane, (△) DEGDEE and (□) acetone

Table 4 State-equation contact energy parameter values X_{12} (J cm^{-3}) between 70° and 140°C

Solute	70	80	90	100	110	120	130	140
n-Hexane	37.4	36.4	35.5	34.7	34.0	33.4	32.9	32.4
n-Octane	20.3	21.5	22.7	24.2	25.7	27.4	29.0	31.0
Benzene	10.1	10.0	10.1	10.6	11.1	12.1	13.1	14.4
Cyclohexane	55.8	53.5	51.4	49.5	47.9	46.3	45.0	43.8
Toluene	13.7	13.5	13.4	13.6	13.9	14.3	15.0	15.8
Methanol	132	130	128	126	125	124	124	124
Ethanol	77.3	73.5	70.0	67.0	64.4	62.3	60.6	59.3
n-Propanol	54.6	50.2	46.6	43.7	41.4	39.7	38.5	37.8
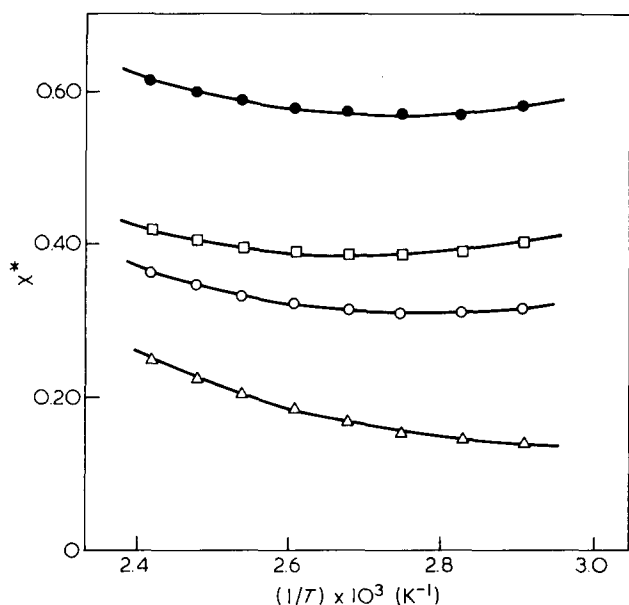
Figure 6 Variation of interaction parameter χ^* with reciprocal temperature (K): (●) ethyl acetate, (□) toluene, (○) benzene and (△) chlorobenzene
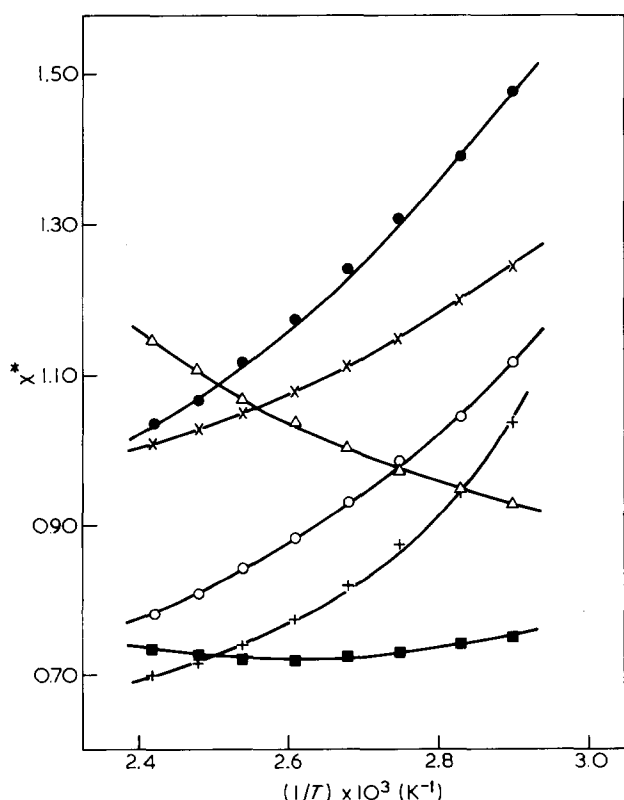
Figure 7 Variation of interaction parameter χ^* with reciprocal temperature (K): (●) cychohexane, (x) methanol, (○) ethanol, (+) n-propanol, (△) n-octane and (■) acetone

which all the components are known. *Table 4* collects the values of X_{12} for eight solutes between 70° and 140°C.

Among the X_{12} data obtained chromatographically, only the values of PEO/toluene and PEO/benzene can be compared with those reported in the literature[15,20] at 60°C. Those values are 1.8 cal cm^{-3} for PEO/toluene and -3 cal cm^{-3} for PEO/benzene, which are in good agreement with those obtained by chromatography, especially in the case of the PEO/toluene system. The negative value for PEO/benzene has been interpreted by Booth and Devoy[15] as a consequence of donor–acceptor complex formation between the benzene (donor) and ether oxygen (acceptor). This explanation seems obscure to us and we think that our chromatographic results, showing similar and positive values for toluene and benzene, are more logical and can be interpreted on the basis of dispersion forces, given its value, similar to those recognized as characteristic of this type of interaction[21].

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