THERMODYNAMICS OF MIXTURES OF AROMATIC HYDROCARBONS WITH ALKANOLS STUDIED BY LIGHT SCATTERING

Petr MUNK[a1,]*, Weizhuang CHENG[a2,+], Anwei QIN[a3,++] and Julius POUCHLÝ[b,]*

[a] *Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin,*
  TX 78712, U.S.A.; e-mail: [1] *p.munk@mail.utexas.edu,* [2] *wzcheng@online.sh.cn,*
  [3] *aqin_98@yahoo.com*
[b] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,*
  162 06 Prague 6, Czech Republic; e-mail: pouchly@imc.cas.cz

Measurement of light scattering of mixtures of aromatic hydrocarbons (benzene, toluene, ethylbenzene) and alkanols (methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol) having sufficiently different refractive indices, produced rather reliable thermodynamic data. From these data it was possible to deduce the composition dependence of the change in Gibbs energy of mixing ΔG_{mix}. These dependences were measured for eleven binary mixtures. A model of alcohol molecules forming linear aggregates which are in equilibrium was developed and used for interpretation of the data. All ΔG_{mix} data for the eleven mixtures as well as the ΔH_{mix} data obtained for these mixtures from literature could be interpreted using just two values that characterized the Gibbs energy and enthalpy of the formation of hydrogen bonds. The analysis also yielded plausible results concerning the contact interactions.
Keywords: Alcohols; Aromatic hydrocarbons; Benzenes; Arenes; Light scattering; Gibbs energy of mixing; Association equilibrium; Thermodynamics; Binary mixtures.

In our previous papers[1–5] we have shown that light scattering can provide valuable thermodynamic data on mixtures of two low-molecular-weight compounds. The data are especially accurate when the refractive indices of the two components differ by about 0.15 or more. Mixtures of aromatic hydrocarbons and alkanols exhibit differences of this magnitude. Alkanols are known to form clusters that are held together by hydrogen bonds. When mixed with other compounds (not capable of hydrogen bonding), the clusters gradually disintegrate. This phenomenon makes the thermodynamics

of mixtures containing alkanols rather complex. In particular, accurate data for Gibbs energy of mixing are generally not available. This study is devoted to collection of such data for the aromatic hydrocarbon/alkanol systems and to their analysis.

Light scattering of a liquid is usually expressed in terms of the Rayleigh ratio. The total scattering Rayleigh ratio, R_t, consists of two parts, isotropic scattering R_{is}, and anisotropic scattering R_{an}. R_t and the intensities of horizontally and vertically polarized scattered light i_h and i_v can be measured experimentally. R_{is} can be evaluated from the relation derived by Cabannes[6].

$$R_{is} = R_t C_f = R_t(6 - 7\Delta)/(6 + 6\Delta) \qquad (1)$$

$$\Delta = i_h/i_v \; , \qquad (2)$$

where C_f is the Cabannes factor, and Δ is the depolarization of the scattered light.

R_{is} can be further divided into the density scattering R_d and the compositional scattering R_c. Hence

$$R_t = R_{is} + R_{an} = R_c + R_d + R_{an} \; . \qquad (3)$$

R_d can be calculated as

$$R_d = \beta(0.5\pi^2 kT/\lambda_0^4)[\rho(\partial\varepsilon/\partial\rho)_T]^2 \; , \qquad (4)$$

where λ_0 is the wavelength of the incident light in vacuum, β is the isothermal compressibility of the liquid, ρ is its density, and ε is its permittivity. ε is equal to n^2 for transparent liquids. The dependence of refractive index n on the liquid density is best represented by the Eykman relation[7,8]. The expression for $\rho(\partial\varepsilon/\partial\rho)_T$ then can be derived as

$$\rho(\partial\varepsilon/\partial\rho)_T = 2n(n + 0.4)(n^2 - 1)/(n^2 + 0.8n + 1) \; . \qquad (5)$$

According to Einstein's theory[9], R_c in a binary mixture of components A and B is related to the chemical potential of the components of the liquid, μ_i as

$$R_c = (2\pi^2 kT/\lambda_0^4)\, V x_A n^2 [(dn/dx_A)^2/(\partial\mu_B/\partial x_B)_{P,T}]\ , \qquad (6)$$

where x_i is the mole fraction of the i-th component (i = A or B), and V is the molar volume of the mixture. In this paper we are going to use the light scattering data for the evaluation of the derivative of the chemical potential $(\partial\mu_B/\partial x_B)_{P,T}$, from which we will obtain ΔG_{mix}, the change of the Gibbs function in the process of mixing. The functional form of ΔG_{mix} for mixtures involving alcohols is quite different from relations typical of mixtures of components that do not exhibit strong specific interactions. We will develop a thermodynamic model of alcohol-containing mixtures that interprets the data quite closely and simultaneously provides new data concerning the thermodynamics of hydrogen bonds.

EXPERIMENTAL

We have analyzed the dependence of light scattering on concentration for eleven binary mixtures of aromatic hydrocarbons and aliphatic linear alcohols. As components of the mixtures we used methanol (ML), ethanol (EL), propan-1-ol (PL), butan-1-ol (BL), pentan-1-ol (AL), benzene (BE), toluene (TO), ethylbenzene (EB), and p-xylene (PX).

The techniques and equipment used for measuring light scattering, density, and refractive index data are the same as those given in our previous paper[1]. All aromatic hydrocarbons and alkanols were obtained from Aldrich Chemical Co. with purity better than 99% and used as supplied. The refractive index of the pure liquids and mixtures were measured with a Bausch–Lomb precision refractometer. The light scattering measurements were performed on a modified Fica 50 photometer equipped with a mercury lamp, and a filter providing incident light at λ_0 = 546 nm. The scattered light was registered with a laboratory photometer (Pacific Instruments Model 110) and its output was measured with a Hewlett–Packard Multimeter (Model 3438A) which was interfaced to a computer. Density was measured with an Anton Paar digital precision density meter (Model DMA 02C). All experiments were performed at 20 °C.

RESULTS AND DISCUSSION

We have evaluated the measured intensities of the scattered light in terms of the total Rayleigh ratio R_t, its anisotropic component R_{an}, the density component R_d, and the compositional Rayleigh ratio R_c. The excess compressibility of the mixtures, which is needed for accurate evaluation of the

density scattering, was not available for our mixtures. However, because the refractive indices for all our solvent pairs were sufficiently different, it was possible[3] to neglect the excess compressibility without unduly compromising the values of R_d. In Table I we are presenting the experimental values of x_B, ϕ_B (volume fraction), R_t, R_{an}, R_c, and $(\partial\mu_B/\partial x_B)_{P,T}$ for our solvent mixtures. We are using subscript A for alcohols and subscript B for aromatic compounds.

As expected, at one end of the composition range, $(\partial\mu_B/\partial x_B)_{P,T}$ increased beyond limits. For easier calculations, we replaced it by a function $F(x)$ defined as

$$(\partial\mu_B/\partial x_B)_{P,T} = RT \, [1/x_B - 2F(x)x_A] \; . \tag{7}$$

It should be noted that the function $F(x)$ is constant and equal to the well-known interaction parameter χ of the van Laar and Flory theories if the mixture could be characterized by χ that is independent of the composition of the mixture. In our present case, $F(x)$ was steeply increasing for low concentrations of the alcohol.

We found it convenient to fit our experimental data to a phenomenological function

$$F(x) = a + bx_B + cx_B^2 + e/x_B \; . \tag{8}$$

The fit was excellent. While the lowest value of $F(x)$ was about 1.1 and the highest values went up to 10, the standard deviation of individual points for all eleven systems was less than 0.15; for seven systems, it was less than 0.07 and for three systems (BE–ML, BE–EL, TO–EL) was less than 0.03.

Using straightforward thermodynamic calculations, we derived from Eqs (7) and (8) first the expressions for the chemical potentials and then the phenomenological relation for ΔG_{mix} which read

$$\Delta G_{mix} = RT \, [x_B \ln x_B + x_A(1 - 2e) \ln x_A + x_A x_B\{a + (b/3)(1 + x_A) +$$

$$(c/6)(1 + x_A + x_A^2)\}] \; . \tag{9}$$

Light scattering data for different mixtures

x_B	ϕ_B	Rayleigh ratio $\cdot 10^4$			$(\partial\mu_B/\partial x_B)_{P,T}$
		R_t	R_{an}	R_c	J/mol
Benzene (B)–methanol (A)					
1.000	1.000	16.694	11.355	0.000	
0.936	0.970	17.315	10.876	1.209	702.3
0.876	0.940	19.624	10.573	3.931	459.2
0.804	0.900	23.848	10.238	8.630	372.1
0.797	0.896	24.735	10.383	9.387	361.0
0.720	0.849	29.605	9.767	15.037	353.0
0.649	0.802	33.918	9.283	19.997	375.6
0.646	0.800	33.661	9.217	19.815	385.1
0.578	0.750	35.573	9.013	22.102	465.9
0.514	0.699	34.103	8.112	21.707	616.1
0.508	0.694	34.460	8.238	21.954	622.4
0.409	0.603	29.715	6.792	18.957	1 057.3
0.407	0.601	29.422	6.856	18.605	1 083.6
0.314	0.501	23.285	5.689	13.956	2 038.6
0.313	0.500	23.912	5.696	14.579	1 958.6
0.231	0.397	17.773	4.717	9.733	3 944.8
0.164	0.302	13.209	3.603	6.564	7 436.9
0.098	0.192	8.869	2.431	3.702	16 776.7
0.000	0.000	2.703	0.462	0.000	
Benzene (B)–ethanol (A)					
1.000	1.000	17.139	11.643	0.000	
0.951	0.967	17.186	11.040	1.178	883.5
0.912	0.941	18.127	10.708	2.523	757.1
0.856	0.901	20.228	10.405	5.034	645.3
0.790	0.851	22.961	9.730	8.570	571.1
0.731	0.805	25.382	9.810	11.029	585.8
0.610	0.704	26.545	8.610	13.643	725.7

x_B	ϕ_B	Rayleigh ratio $\cdot 10^4$			$(\partial\mu_B/\partial x_B)_{P,T}$
		R_t	R_{an}	R_c	J/mol
0.502	0.605	24.002	7.258	12.686	1 048.8
0.403	0.507	20.022	6.375	9.815	1 703.0
0.308	0.404	15.861	5.128	7.122	2 853.4
0.227	0.308	12.069	3.938	4.720	4 986.8
0.149	0.210	8.848	2.999	2.634	10 242.9
0.066	0.097	5.625	1.573	1.052	29 543.4
0.000	0.000	3.336	0.515	0.000	
		Benzene (B)–propan-1-ol (A)			
1.000	1.000	16.700	11.348	0.000	
0.960	0.996	16.771	11.032	0.494	1 695.9
0.885	0.901	18.474	10.440	2.986	793.2
0.802	0.828	19.888	9.437	5.618	717.8
0.728	0.761	21.217	9.016	7.557	733.0
0.640	0.679	21.503	8.428	8.651	851.8
0.549	0.592	19.177	7.147	7.830	1 193.5
0.443	0.486	16.103	5.454	6.710	1 762.7
0.348	0.388	13.118	4.238	5.175	2 751.4
0.258	0.292	10.203	3.357	3.359	4 952.1
0.089	0.104	5.798	1.703	1.015	20 996.4
0.000	0.000	3.353	0.483	0.000	
		Benzene (B)–butan-1-ol (A)			
1.000	1.000	16.700	11.463	0.000	
0.969	0.969	16.998	11.120	0.731	1 045.2
0.938	0.936	17.419	10.644	1.715	882.0
0.907	0.904	18.040	10.492	2.572	854.7
0.845	0.841	18.964	9.810	4.341	798.5
0.766	0.761	19.571	9.015	5.939	827.6
0.683	0.676	19.224	8.271	6.533	963.3

T ABLE I
(*Continued*)

x_B	ϕ_B	Rayleigh ratio $\cdot 10^4$			$(\partial\mu_B/\partial x_B)_{P,T}$
		R_t	R_{an}	R_c	J/mol
0.593	0.586	17.534	7.260	6.056	1 263.8
0.495	0.488	15.067	5.586	5.473	1 648.5
0.394	0.387	12.285	4.584	3.899	2 654.6
0.300	0.293	9.792	3.723	2.452	4 701.4
0.201	0.196	7.600	2.549	1.619	7 842.8
0.107	0.104	5.617	1.572	0.783	17 580.6
0.000	0.000	3.634	0.556	0.000	
		Benzene (B)–pentan-1-ol (A)			
1.000	1.000	16.700	11.253	0.000	
0.959	0.951	16.974	10.820	0.878	1 296.8
0.919	0.903	17.713	10.432	2.167	984.3
0.865	0.840	18.427	9.873	3.640	896.3
0.794	0.759	18.889	9.506	4.715	957.3
0.714	0.672	18.116	8.308	5.391	1 044.3
0.628	0.580	16.324	7.478	4.676	1 410.5
0.532	0.483	14.126	6.072	4.133	1 799.0
0.434	0.386	11.842	4.867	3.285	2 468.5
0.329	0.287	9.239	3.439	2.333	3 717.8
0.226	0.193	7.393	2.618	1.507	6 044.3
0.098	0.082	5.459	1.818	0.595	15 988.0
0.000	0.000	3.567	0.679	0.000	
		Toluene (B)–ethanol (A)			
1.000	1.000	19.411	14.682	0.000	
0.939	0.966	19.788	13.884	1.226	705.9
0.885	0.933	20.908	13.413	2.864	603.1
0.820	0.892	23.359	13.220	5.570	520.8
0.736	0.835	25.629	11.876	9.271	502.9
0.663	0.782	27.437	11.044	11.995	542.9

x_B	ϕ_B	Rayleigh ratio $\cdot 10^4$			$(\partial\mu_B/\partial x_B)_{P,T}$
		R_t	R_{an}	R_c	J/mol
0.578	0.714	28.152	10.284	13.578	672.8
0.484	0.631	26.849	9.095	13.604	945.4
0.382	0.530	22.524	7.497	11.053	1 648.8
0.296	0.434	18.396	5.678	8.919	2 719.3
0.219	0.339	14.104	4.333	6.151	5 050.3
0.148	0.241	10.619	3.042	4.146	9 357.0
0.000	0.000	3.493	0.529	0.000	
		Toluene (B)–propan-1-ol (A)			
1.000	1.000	19.457	14.752	0.000	
0.954	0.967	20.162	14.577	0.938	767.3
0.912	0.937	20.161	13.649	1.919	730.6
0.868	0.903	20.386	12.966	2.884	744.5
0.789	0.841	21.915	12.197	5.287	671.5
0.696	0.765	23.204	11.440	7.461	721.3
0.608	0.688	23.190	10.310	8.706	845.0
0.500	0.587	21.201	8.959	8.235	1 243.5
0.403	0.490	18.210	7.255	7.109	1 880.0
0.307	0.387	13.646	4.270	5.704	2 997.5
0.227	0.294	11.110	3.943	3.652	5 685.2
0.151	0.202	8.776	2.840	2.577	9 546.1
0.000	0.000	3.585	0.565	0.000	
		Toluene (B)–butan-1-ol (A)			
1.000	1.000	19.565	14.589	0.000	
0.945	0.952	19.712	13.968	0.895	1 106.7
0.890	0.904	20.203	13.232	2.247	871.7
0.820	0.841	20.607	12.211	3.826	828.4
0.730	0.759	20.852	10.903	5.576	850.6
0.643	0.676	20.303	9.929	6.190	1 019.8

| x_B | ϕ_B | Rayleigh ratio $\cdot 10^4$ | | | $(\partial\mu_B/\partial x_B)_{P,T}$ |
		R_t	R_{an}	R_c	J/mol
0.547	0.584	18.504	8.534	5.986	1 353.8
0.447	0.484	15.909	6.964	5.173	1 958.4
0.349	0.384	13.929	5.864	4.497	2 725.9
0.258	0.287	11.058	4.055	3.624	3 972.8
0.083	0.095	6.042	1.986	1.035	8 185.1
0.000	0.000	3.477	0.623	0.000	
		Toluene (B)–pentan-1-ol (A)			
1.000	1.000	19.436	14.521	0.000	
0.953	0.952	19.564	13.944	0.817	1 144.7
0.904	0.903	20.016	13.437	1.889	974.2
0.844	0.842	20.137	12.321	3.260	882.1
0.760	0.756	19.818	11.156	4.287	985.1
0.680	0.676	19.278	10.339	4.729	1 143.8
0.591	0.587	17.343	8.728	4.578	1 452.3
0.490	0.485	15.176	7.372	3.958	2 026.4
0.393	0.388	12.651	5.842	3.140	2 963.6
0.289	0.286	10.030	3.925	2.617	4 067.0
0.204	0.201	7.965	3.104	1.517	7 739.0
0.095	0.094	5.669	1.840	0.661	19 809.3
0.000	0.000	3.668	0.652	0.000	
		Ethylbenzene (B)–ethanol (A)			
1.000	1.000	17.226	12.657	0.000	
0.932	0.966	17.731	12.227	0.992	841.8
0.870	0.933	19.201	11.796	2.949	587.9
0.811	0.900	21.078	11.235	5.444	500.9
0.704	0.833	25.578	10.411	10.883	463.3
0.630	0.781	28.831	10.283	14.356	497.8
0.529	0.702	30.153	9.203	16.899	643.4

TABLE I
(*Continued*)

x_B	ϕ_B	Rayleigh ratio $\cdot 10^4$			$(\partial\mu_B/\partial x_B)_{P,T}$
		R_t	R_{an}	R_c	J/mol
0.424	0.607	27.975	7.953	16.143	1 006.8
0.354	0.535	24.640	6.993	13.900	1 518.9
0.219	0.370	16.975	3.698	9.841	3 548.4
0.134	0.246	11.071	2.742	5.131	9 325.5
0.085	0.163	8.445	1.794	3.610	15 952.8
0.000	0.000	3.137	0.406	0.000	
		p-Xylene (B)–ethanol (A)			
1.000	1.000	25.275	20.666	0.000	
0.870	0.934	26.543	19.319	2.730	617.4
0.815	0.903	28.336	18.651	5.246	497.2
0.700	0.831	31.605	16.776	10.519	482.7
0.583	0.747	34.787	14.873	15.756	547.8
0.485	0.666	33.127	12.682	16.437	777.7
0.397	0.582	29.427	10.605	14.971	1 198.7
0.307	0.483	24.244	8.799	11.782	2 141.2
0.228	0.384	18.874	6.856	8.546	3 981.7
0.160	0.288	14.284	3.555	7.445	5 928.0
0.101	0.191	10.218	3.064	4.059	13 773.1
0.049	0.098	6.412	1.647	1.854	37 190.8
0.000	0.000	3.207	0.489	0.000	

The values of *a*, *b*, *c*, and *e* are collected in Table II.

A full thermodynamic analysis of the process of mixing requires experimental data for ΔG_{mix} as well as for the change of the enthalpy of mixing ΔH_{mix}, and of the volume of mixing ΔV_{mix}. Fortunately, the enthalpies of mixing ΔH_{mix} of ten of our eleven systems were measured by Mrazek and Van Ness[10] at 25, 35, and 45 °C. We have extrapolated their smoothed values to our experimental temperature of 20 °C. The result can be described by Eq. (*10*); the applicable values of the parameters are collected in Table III.

TABLE II
Coefficients for the fitting of the dependence of the function $F(x)$ on composition (Eq. (*8*)) and for calculating the dependence of ΔG_{mix} on composition (Eq. (*9*))

Mixture	*a*	*b*	*c*	*e*
BE–ML	1.5162	–1.7821	2.0376	.3017
BE–EL	1.3522	–1.4592	1.5089	.2821
BE–PL	3.6002	–7.4420	5.6233	.0425
BE–BL	1.5163	–2.6841	2.2305	.2587
BE–AL	2.6054	–7.0615	6.7746	.1618
TO–EL	1.1375	–1.0230	1.4362	.3219
TO–PL	0.7818	–0.3061	0.8167	.3310
TO–BL	2.4156	–6.3636	6.7046	.1865
TO–AL	1.5926	–3.0286	2.7003	.2221
EB–EL	2.3395	–5.0760	5.5525	.2250
PX–EL	1.7052	–3.4316	4.2717	.2875

TABLE III
Coefficients for dependence of ΔH_{mix} on x_B at 20 °C (Eq. (*10*))

Mixture	$10^4 A$	$10^4 B$	$10^4 C$	$10^4 D$	$10^4 E$	$10^4 F$
BE–ML	4.3572	2.6747	–0.4607	0.4182	–0.0186	0.1271
BE–EL	3.5786	2.3892	0.3217	0.8408	–0.0533	–0.0312
BE–PL	2.8469	1.6514	0.2873	0.6070	–0.2561	0.0349
BE–BL	2.5556	1.4767	0.3682	0.4800	–0.2975	0.1127
BE–AL	2.4753	1.3659	0.2961	0.3122	–0.2913	0.2473
TO–EL	3.8624	2.4995	0.2422	0.9490	0.0539	0.1004
TO–PL	3.0959	1.9947	0.3157	0.4567	–0.2174	0.1481
TO–BL	2.8903	1.7764	0.3548	0.5076	–0.1688	0.2625
TO–AL	3.2104	1.7361	0.3179	0.5392	–0.1628	0.2658
EB–EL	3.5176	2.1063	–0.0658	0.5216	–0.2145	0.0224

$$\Delta H_{mix} = x_A x_B / [A + B(1 - 2x_B) + C(1 - 2x_B)^2 + D(1 - 2x_B)^3 + E(1 - 2x_B)^4 + \quad (10)$$
$$F(1 - 2x_B)^5]$$

In our previous paper[11] we have reported measurement of ΔV_{mix} for a majority of our systems. The results are represented by Eq. (*11*) and the parameters are presented in Table IV.

$$\Delta V_{mix} = x_A x_B [a_0 + a_1(x_B - x_A)] / [1 + c(x_B - x_A)] \qquad (11)$$

Neither the van Laar theory, which is applicable to mixtures of small molecules, nor the Flory–Huggins theory developed for mixtures of molecules differing appreciably in size were capable of interpreting the experimental data. Especially vexing was the role of the parameter *e* in Eq. (*9*). We have therefore developed a model of the thermodynamic behavior of liquid alcohols and their mixtures with hydrocarbons and similar molecules.

TABLE IV
Coefficients for dependence of ΔV_{mix} on x_B at 20 °C (Eq. (*11*))

Mixture	a_0	a_1	c
BE–ML	–0.030	0.217	–0.086
BE–EL	0.026	0.646	–0.210
BE–PL	0.285	0.521	–0.346
BE–BL	0.660	0.360	–0.280
BE–AL	0.984	0.187	–0.383
TO–EL	–0.323	0.731	0.045
TO–PL	–0.151	0.758	–0.040
TO–BL	0.090	0.600	–0.169
TO–AL	0.189	0.442	–0.359
EB–EL	–0.046	0.640	–0.143
PX–EL	–0.185	0.649	0.196

Model of Liquid Alcohols and Their Mixtures with Hydrocarbons

It is well known that water molecules are bound by hydrogen bonds into an ever-changing three-dimensional network. In liquid alcohols, hydrogen bonds act in a similar way. However, each alcohol molecule has only one hydroxy group capable of hydrogen bonding. Thus, the resulting aggregates are linear. In the liquid exist chains having various numbers of monomeric units. These chains are in a fast equilibrium. When a compound incapable of participating in hydrogen bonds dilutes the alcohol, the equilibrium distribution of the chain length has to shift. In the literature, there are numerous studies of these issues, some of them quite similar to our model[12–16]. Nevertheless, we deem it important to present our analysis in detail because of some finer points that are crucial for interpreting our experimental data.

In our model we will assume that standard relations in the thermodynamics of chemical reactions can describe the equilibrium. We will also consider the role played by the configuration statistics of liquid solutions. Following the Flory–Huggins theory, we will use the quasi-crystalline lattice model of liquids and employ the Boltzmann relation for calculating the configuration entropy of the mixtures. In a snapshot view, the alcohol chains resemble a polydisperse polymer and we will treat them as such. In the following, we will consider all chains as molecules of separate chemical species. We will often call them *i*-mers.

Our goal is to evaluate ΔH_{mix}, ΔS_{mix}, and ΔG_{mix} for mixtures of alcohols and diluents starting from the properties of molecules and from their behavior in the hydrogen bonding and in the contact interactions. The conformational behavior of the molecules plays a major role in our model. We will divide the conformational changes into two groups. In one group, the change of conformation does not affect the shape of the molecules enough to influence the placement of the molecule on the lattice (*e.g.*, rotations of the methyl groups). We will call these conformations *internal conformations*. In the other group, the change of conformation changes the shape of the molecule and therefore its placement on the lattice. It is customary in the pseudocrystalline lattice theories of solutions to model the multiple conformations by dividing the molecules into segments that can be placed on the lattice as a continuous chain. The resulting conformations are *external conformations*.

In the first step of our analysis we need to accommodate our molecules A and B which have generally a different size to a common lattice. In standard studies it is usual to divide each molecule into segments of the same size. There are r_A and r_B of them. These quantities usually do not figure in-

dividually in the final expressions. Thus they may be selected arbitrarily, only their ratio must be equal to the ratio of molar volumes. However, we will eventually see that in the present case the individual values do matter.

We found it convenient to define rigid molecules as molecules having only internal degrees of freedom characterized by *internal conformational partition function Y*. We will consider several liquids. Hypothetical rigid pure monomeric alcohol (as well as diluent) is a collection of rigid alcohol unimers placed on the lattice in a unique way. Pure rigid aggregated alcohol is a collection of chains of alcohol entities still in the rigid form and still uniquely placed on the lattice. Collections having two distributions of chain lengths are considered: one corresponding to the alcohol in its pure form, the other to its mixture with the diluent. The following subscripts are used: A for quantities related to all alcohol entities, B for diluent molecules, and *i* for individual *i*-mers.

In the next step we ascribe to our rigid molecules basic values of enthalpy H_A and H_B, of entropy S_A and S_B, and internal conformational partition function Y_A and Y_B. The H and S values reflect mainly the chemical structure of the molecules. $(i - 1)$ hydrogen bonds arise when rigid *i*-mers are formed from *i* rigid molecules of the alcohol. We assume that each hydrogen bond contributes H_H, S_H, and Y_H to the enthalpy H_i, entropy S_i, and partition function Y_i of the rigid *i*-mers, respectively. Thus

$$H_i = iH_A + (i - 1)H_H \tag{12}$$

$$S_i = iS_A + (i - 1)S_H \tag{13}$$

$$Y_i = Y_A^i Y_H^{(i-1)} \tag{14}$$

The basic values of H_A, H_B, S_A, S_B, Y_A, and Y_B do not depend on the state of the system, *i.e.*, whether it is a pure component or a mixture, whether rigid or accommodated on the lattice. They will not enter the final expressions, only H_H, S_H, and Y_H will.

We consider a system composed of N_A alcoholic entities and N_B molecules of the diluent that are randomly placed on a lattice with $N = r_A N_A + r_B N_B$ lattice points. The alcoholic entities are distributed among *i*-mers. The

number of individual i-mers is N_i; each molecule of an *i*-mer occupies ir_A lattice points. Obviously, $\Sigma_i\, iN_i = N_A$. We also define volume fractions as $\phi_A = r_A N_A/N$, $\phi_B = r_B N_B/N$, and $\phi_i = ir_A N_i/N$.

We need to evaluate enthalpy and entropy values for pure diluent (subscript d), pure alcohol (subscript alc), and the mixture (subscript m). Evaluation of the enthalpy values is straightforward:

$$H_d = N_B H_B \tag{15}$$

$$H_{alc} = \Sigma_i\, N_i^0 H_i = N_A(H_A + H_H) - \Sigma_i\, N_i^0 H_H \tag{16}$$

$$H_m = N_B H_B + \Sigma_i\, N_i H_i + H_{cont} = N_B H_B + N_A(H_A + H_H) - \Sigma_i\, N_i H_H + H_{cont}\,. \tag{17}$$

Here, H_{cont} is the enthalpy part of the contact interaction term. We will return to it later.

Evaluation of the entropy values is more complicated. Entropy consists of three terms:

1. Chemical structure related entropy (subscript st) that is quite analogous to enthalpy

$$S_{d,st} = N_B S_B \tag{18}$$

$$S_{alc,st} = N_A(S_A + S_H) - \Sigma_i\, N_i^0 S_H \tag{19}$$

$$S_{m,st} = N_B\, S_B + N_A(S_A + S_H) - \Sigma_i\, N_i S_H\,. \tag{20}$$

2. Internal conformation related term (subscript int). For this term we will use the Boltzmann relation that in the present case yields

$$S_{d,int} = k\, \ln Y_B^{N_B} = kN_B\, \ln Y_B \tag{21}$$

$$S_{\text{alc,int}} = k \, \Sigma_i \, N_i^0 \, \ln \, Y_i = k(N_A \ln Y_A + N_A \ln Y_H - \Sigma_i \, N_i^0 \, \ln Y_H) \qquad (22)$$

$$S_{\text{m,int}} = k(N_B \ln Y_B + \Sigma_i \, N_i \ln Y_i) = k(N_B \ln Y_B + N_A \ln Y_A + N_A \ln Y_H - \qquad (23)$$
$$\Sigma_i \, N_i \ln Y_H)$$

3. External conformation term. This is the term usually employed in pseudolattice theories. In our model it is related to W, the number of different microscopic on-lattice arrangements compatible with the same macroscopic state of the system by the Boltzmann relation $S = k \ln W$. We will first evaluate W for the mixture, then calculate the expressions for the diluent and the alcohol as limits for vanishing values of N_A and N_B, respectively.

The expression for W for our system reads

$$W = \frac{N!}{N_B! \, N^{(r_B - 1)N_B + \Sigma_i (ir_A - 1)N_i} \prod_i N_i!} W_{\text{ext}} \,, \qquad (24)$$

where $N = (N_A r_A + N_B r_B)$ is the number of lattice points and the term W_{ext} is due to multiplicity of external chain conformations. For W_{ext}, Eq. (*24a*) holds.

$$W_{\text{ext}} = \exp (S_{\text{m,ext}}/k) \qquad (24a)$$

Here $S_{\text{m,ext}}$ is defined by modified Eq. (*23*), where we have replaced the subscript "int" by "ext" and the indexed symbols Y by identically indexed symbols X. For example, the symbol X_i denotes the number of possible i-mer external conformations, *i.e.* the number of ways of placing an *i*-mer on an empty lattice if the position of one of its end segments is fixed. Stirling approximation of factorials and routine algebra transform Eq. (*24*) into

$$S_{\text{m,conf}}/k = N_B - N_B r_B + \Sigma_i \, N_i - N_A r_A - N_B \ln (\phi_B/r_B) - \Sigma_i \, N_i \ln (\phi_i/ir_A) + \qquad (25)$$
$$S_{\text{m,ext}}/k \,.$$

Conformational entropies for pure diluent and pure alcohol are then found as

$$S_{d,conf}/k = N_B - N_B r_B + N_B \ln r_B + S_{d,ext}/k \qquad (26)$$

$$S_{alc,conf}/k = \Sigma_i N_i^0 - N_A r_A - \Sigma_i N_i^0 \ln (\phi_i^0/i r_A) + S_{alc,ext}/k . \qquad (27)$$

The superscript zero in N_i^0 and ϕ_i^0 refers to the distribution of chain length in pure alcohol that is different from the distribution of alcohol chains in their mixtures with the diluent.

The change of entropy in mixing ΔS_{mix} is then calculated by subtracting the values for pure diluent and pure alcohol from the values of the mixture. For the three entropy terms, we then obtain after some manipulation

$$\Delta S_{mix,st} = (\Sigma_i N_i^0 - \Sigma_i N_i)S_H \qquad (28)$$

$$\Delta S_{mix,int} = k(\Sigma_i N_i^0 - \Sigma_i N_i) \ln Y_H \qquad (29)$$

$$\Delta S_{mix,conf} = k[-N_B \ln \phi_B + \Sigma_i N_i^0 \ln (\phi_i^0/i) - \Sigma_i N_i \ln (\phi_i/i) - \qquad (30)$$
$$(\Sigma_i N_i^0 - \Sigma_i N_i)(1 + \ln r_A) + (\Sigma_i N_i^0 - \Sigma_i N_i) \ln X_H] .$$

Combining the applicable terms, we obtain

$$\Delta S_{mix} = (\Sigma_i N_i^0 - \Sigma_i N_i)[S_H + k(\ln Z_H - 1 - \ln r_A)] + \qquad (31)$$
$$k[-N_B \ln \phi_B + \Sigma_i N_i^0 \ln (\phi_i^0/i) - \Sigma_i N_i \ln (\phi_i/i)] + S_{cont} ,$$

where

$$Z_H = Y_H X_H \qquad (31a)$$

is the contribution of one hydrogen bond to the total (*i.e.* both internal and external) conformational partition function Z_i. The last term S_{cont} in Eq. (*31*) is the entropy part of the contact interaction term. Similar combination of enthalpy terms leads to ΔH_{mix}.

$$\Delta H_{mix} = (\Sigma_i N_i^0 - \Sigma_i N_i)H_H + H_{cont} \tag{32}$$

Finally, for $\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$ we get

$$\Delta G_{mix} = (\Sigma_i N_i^0 - \Sigma_i N_i)[H_H - TS_H - kT (\ln Z_H - 1 - \ln r_A)] + \tag{33}$$
$$kT [N_B \ln \phi_B - \Sigma_i N_i^0 \ln (\phi_i^0/i) + \Sigma_i N_i \ln (\phi_i/i)] + G_{cont}$$

In the last term, we combined the contact terms as $G_{cont} = H_{cont} - TS_{cont}$.

The expressions (*31*)–(*33*) are general in the sense that they apply whatever are the distributions of N_i^0 and N_i. However, we are looking for more practical relations that are based on the equilibria governing the creation/destruction of hydrogen bonds and are hopefully more simple. For this purpose, we need to know the chemical potentials of the *i*-mers μ_i. We will evaluate them from their definition

$$\mu_i = [\partial G_m/\partial n_i]_{P,T,nj\neq i} = N_{Av}[\partial G_m/\partial N_i]_{P,T,Nj\neq i} . \tag{34}$$

In this relation n_i is the number of moles of the *i*-th component, N_{Av} is the Avogadro constant, and G_m is the Gibbs energy of the mixture, which is related to previously calculated quantities as

$$G_m = H_m - T(S_{m,st} + S_{m,int} + S_{m,conf} + S_{cont}) = \tag{35}$$
$$N_B[H_B - T\{S_B + k(\ln Z_B - \ln \phi_B + \ln r_B + 1 - r_B)\}] +$$
$$N_A[H_A + H_H - T\{S_A + S_H + k(\ln Z_A + \ln Z_H - r_A)\}] +$$
$$\Sigma_j N_j[-H_H - T\{-S_H + k(- \ln Z_H + 1 - \ln \phi_j + \ln jr_A)\}] + G_{cont} .$$

For the purpose of taking the derivative, it was convenient to switch the summation index from *i* to *j*. We need also to express G_{cont} in an analytical form. We will follow the Flory–Huggins approach by approximating the term by a product of estimated number of contacts between species A and

B, $N_B\phi_A$, and the parameter $RTg(\phi_B)$ characterizing the interactions between molecules A and B. We allow the parameter $g(\phi_B)$ to depend on the composition of the mixture, because such dependence has been observed in many experimental systems.

Before taking the derivative, it is practical to recognize the following relations that are valid for our model.

$$\partial N_A/\partial N_i = i \tag{36}$$

$$\partial \ln \phi_B/\partial N_i = - i\phi_A/N_A \tag{37}$$

$$\partial \Sigma_j N_j \ln \phi_j/\partial N_i = \ln \phi_i + 1 - i \Sigma_j \phi_j/j \tag{38}$$

$$\partial G_{cont}/\partial N_i = (ikT\phi_B^2 r_A/r_B)(g - \phi_A\partial g/\partial \phi_B) \tag{39}$$

We are omitting the constancy subscripts in the above and following expressions. With the help of these relations, the required relation for μ_i is obtained as

$$\mu_i/N_{Av} = i[H_A + H_H - TS_A - TS_H - \tag{40}$$
$$- kT\{\ln Z_A + \ln Z_H - r_A + \phi_A/N_A + \Sigma_j \phi_j/j - (\phi_B^2 r_A/r_B)(g - \phi_A(\partial g/\partial \phi_B))\}] -$$
$$H_H + TS_H + kT \ln Z_H + kT \ln (\phi_i/ir_A) .$$

We are now ready to study the equilibrium of reactions involving hydrogen bonds. Let us consider the following reaction between an i-mer A_i and an unimer A_1.

$$A_i + A_1 \rightleftarrows A_{i+1} \tag{41}$$

At equilibrium, the following relation must hold

$$\mu_i + \mu_1 - \mu_{i+1} = 0 . \tag{42}$$

We will substitute into this relation sequentially the expressions for chemical potentials from Eq. (*40*) adapted for unimer, *i*-mer, and (*i* + 1)-mer. The terms that in Eq. (*40*) are multiplied by *i* will cancel out and Eq. (*42*) will change to

$$N_{Av}(-H_H + TS_H + kT \ln Z_H - kT \ln r_A) = RT \ln [i\phi_{i+1}/(i + 1)\phi_i\phi_1] . \quad (43)$$

Let us define standard Gibbs energy for formation of hydrogen bonds G^0 and equilibrium constant K as

$$G^0 \equiv N_{Av}(H_H - TS_H - kT \ln Z_H + kT \ln r_A) \quad (44)$$

$$K \equiv \exp (-G^0/RT) . \quad (45)$$

It is noteworthy that G^0 contains, besides the quantities that characterize the hydrogen bond, also the parameter r_A that describes the size of the alcohol molecule.

Equation (*43*) may be now recast as

$$\phi_{i+1} = [(i + 1)\phi_1/i]K\phi_i . \quad (46)$$

Substituting an analogous expression for ϕ_i into Eq. (*44*) and repeating it again and again, we obtain a relation that expresses the whole distribution of *i*-mers in terms of ϕ_1, namely

$$\phi_i = iK^{i-1}\phi_1^i . \quad (47)$$

For calculating ϕ_1, we use the mass balance equation which reads

$$\phi_A = \Sigma_i \phi_i = \phi_1\Sigma_i i(K\phi_1)^{i-1} = \phi_1/(1 - K\phi_1)^2 . \quad (48)$$

Solving the last equation in Eq. (*48*) yields

$$\phi_1 = [2K\phi_A + 1 - \{(2K\phi_A + 1)^2 - 4K^2\phi_A^2\}^{1/2}]/2K^2\phi_A \ . \tag{49}$$

When considering pure alcohol in the absence of the diluent, we obtain a similar expression

$$\phi_1^0 = [2K + 1 - \{(2K + 1)^2 - 4K^2\}^{1/2}]/2K^2 \ . \tag{50}$$

The rest of the calculation is straightforward. We modify Eq. (*33*) for ΔG_{mix} by expressing N_i^0 and N_i first in terms of ϕ_i^0 and ϕ_i and then in terms ϕ_1^0 and ϕ_1. The summations follow from known algebraic rules. Finally, we recast the equation in terms of moles instead of molecules, introduce G^0 as in Eq. (*44*), and enter our model representation of G_{cont}. The result reads

$$\begin{aligned}
\Delta G_{\text{mix}} = - &[G^0 + RT]n_A[\phi_1/\{\phi_A(1 - K\phi_1)\} - \phi_1^0/(1 - K\phi_1^0)] + \\
&RT[n_A\phi_1/\{\phi_A(1 - K\phi_1)\}][\ln (K\phi_1)/(1 - K\phi_1) - \ln K] - \\
&RT[n_A\phi_1^0/(1 - K\phi_1^0)][\ln (K\phi_1^0)/(1 - K\phi_1^0) - \ln K] + \\
&RT \, n_B \ln \phi_B + RT \, n_B\phi_A \, g(\phi_B) \ .
\end{aligned} \tag{51}$$

Further manipulation of this equation leads to a much simpler form.

$$\Delta G_{\text{mix}} = n_A \, RT[\ln (\phi_1/\phi_1^0) + K(\phi_1 - \phi_1^0)] + RT \, n_B \ln \phi_B + RT \, n_B\phi_A \, g(\phi_B) \tag{52}$$

Of course, the quantities ϕ_1 and ϕ_1^0 must be obtained from Eqs (*49*) and (*50*).

Manipulations analogous to those that transformed Eq. (*33*) into Eq. (*52*) when applied to Eq. (*32*) give for ΔH_{mix}

$$\Delta H_{\text{mix}} = n_A N_{\text{Av}} \, K(\phi_1 - \phi_1^0)H_H + RT \, n_B\phi_A \, h(\phi_B) \ , \tag{53}$$

where $h(\phi_B)$ is the enthalpy part of the Gibbs energy function $g(\phi_B)$.

Thus for our model, both ΔG_{mix} and ΔH_{mix} are expressed as functions of two constant parameters K (or G^0) and $H^0 = N_{Av}H_H$, and two functions of the composition of the mixture $g(\phi_B)$ and $h(\phi_B)$.

In the next section, we will try to evaluate these parameters and functions from our experimental data.

Interpretation of the Experimental Data

In the first step of our analysis we will be asking whether our model of alcohol–diluent mixtures is capable of describing our experimental data with a reasonable accuracy. In the next step, we will try to calculate the basic thermodynamic quantities governing our system.

The experimental data for the dependence of ΔG_{mix} on composition are to be fitted by an adjustable parameter G^0 and an adjustable function $g(\phi_B)$. It is obvious that for every arbitrary value of G^0 there exists a function $g(\phi_B)$ that yields a good fit. Consequently, we need to develop some criterion that restricts the range of acceptable values of our adjustable quantities. We will require that $g(\phi_B)$ be a slowly varying function that does not exhibit sharp turns on either end of the concentration scale. We have found that, for a given binary system, this criterion is satisfied for only a narrow range of G^0 values.

We have performed the above analysis for all our experimental systems and collected a list of the most plausible values of G^0. We have found that the G^0 values were very close for mixtures containing the same alcohol and depended on the length of the alcohol in a very regular way. Equation (*44*) predicts that for different alcohols, G^0 is a linear function of $RT \ln r_A$, where r_A is the number of lattice locations occupied by the alcohol molecule. A plausible assumption would make r_A equal to the number of atom groups contributed by the alcohol to the chain, that is $r_A = 2$ for methanol, $r_A = 3$ for ethanol, and so on. We have therefore adjusted the G^0 values to satisfy Eq. (*44*). The necessary adjustments were only minor. The adjusted values satisfied the relation

$$G^0 = -13\ 380 \text{ J/mol} + RT \ln r_A \ . \tag{54}$$

Using the adjusted values we have recalculated the $g(\phi_B)$ functions. They still behaved well. Table V collects the values of G^0 and of the function $g(\phi_B)$ at its midpoint, *i.e.*, at $\phi_B = 0.5$. Most functions $g(\phi_B)$ were very flat; the dif-

ference between the lowest and highest value in the interval $\phi_B = 0.05$ to 0.95 was less than 0.2 for seven of them; for none was it higher than 0.8. We ascribe this slightly erratic shape of the function to the experimental and fitting errors in our light scattering data. These errors influence the data most seriously at the ends of the concentration scale. It was most satisfying that the g values behaved in a very regular way with respect to the length of the alcohol molecule.

Once the value of G^0 is fixed, ΔH_{mix} may be fitted by an adjustable parameter H^0 and an adjustable function $h(\phi_B)$. Using again the same approach, we have found again that only a narrow range of H^0 values yields a slowly varying function $h(\phi_B)$. For all our systems, the H^0 values were very close to each other. In the next step we repeated the fitting procedure, but we adopted for all our system the same value of $H^0 = -27\ 000$ J/mol. The values of $h(\phi_B)$ at $\phi_B = 0.5$ exhibited a dependence on the length of the alcohol molecule that was less satisfactory but still acceptable in our eyes: with one exception, the difference between the lowest and highest value in the interval $\phi_B = 0.05-0.95$ was less than 0.3. The values of $h(\phi_B)$ at $\phi_B = 0.5$ are included in Table V.

TABLE V
Thermodynamic results for eleven alcohol–aromatic hydrocarbon mixtures

Mixture	G^0, kJ/mol	$g(\phi_B = 0.5)$	$h(\phi_B = 0.5)$
BE–ML	–11.69	0.20	–0.26
BE–EL	–10.70	0.27	–0.10
TO–EL	–10.70	0.24	–0.26
EB–EL	–10.70	0.28	–0.27
PX–EL	–10.70	0.27	
BE–PL	–10.00	0.29	0.25
TO–PL	–10.00	0.30	–0.03
BE–BL	–9.46	0.40	0.54
TO–BL	–9.46	0.41	0.15
BE–AL	–9.01	0.55	0.73
TO–AL	–9.01	0.35	0.11

The observed dependence of the g values on the size of the alcohol molecule is not unexpected. In our previous studies[4,17] we have observed that there exists a specific interaction between aromatic rings and oxygen-carrying compounds (ketones, esters). This explains the very low interaction coefficients for the shorter alcohols. The longer alcohols carry a much longer aliphatic segment, the interaction of which with aromatic compounds is known to lead to moderately positive values of the interaction coefficient g. The negative values of the enthalpy portion h of the interaction coefficient that were observed for the shorter alcohols are consistent with the surmised specific interaction of the alcoholic oxygen with the aromatic ring. Moreover, their comparison with the Gibbs energy coefficient g leads to the conclusion that the entropy in our mixtures decreases due to the formation of contacts between the alcohol chains and the aromatic molecules. Again, this should not be surprising: the aromatic molecules that have to approach the alcohol oxygen in a proper way must lose part of their entropy because their orientation becomes less random.

Renon and Prausnitz[12] analyzed literature data (calorimetry, vapor–liquid equilibria) for mixtures of alcohols with aliphatic hydrocarbons. They also found that H^0 is the same for all alcohols and report for it a value of –7.5 kcal/mol (–31.4 kJ/mol). This is a close agreement with our value –27 kJ/mol. For measurements at 50 °C, they report for the equilibrium constant K the value 350 for methanol, 150 for ethanol, and 70 for propan-1-ol. Our values for these compounds at 20 °C are 120, 80, and 60, respectively.

The volume fraction ϕ_i is in common use in treatments based on the Flory–Huggins theory. One of us[16] has shown that the association equilibrium constant is virtually independent of r_A if defined in terms of the concentration ψ_i

$$\psi_i = N_i/N = \phi_i/ir_A \tag{55}$$

The new equilibrium constant K_ψ is

$$K_\psi = \psi_{i+1}/(\psi_i \psi_1) = r_A \, K \tag{56}$$

and the corresponding standard Gibbs energy G_ψ^0

$$G_\psi^0 = G^0 - RT \ln r_A \tag{57}$$

so that from Eq. (*54*) we have

$$G_\psi^0 = -13\ 380 \text{ J/mol} \tag{58}$$

irrespective of the alcohol chain length. This is understandable because ψ_i is proportional to the molar concentration of *i*-mers c_i, and so also to the frequency of free hydrogen atoms of hydroxy groups situated at the end of each *i*-mer chain.

What is the value of entropy accompanying the formation of the hydrogen bonds? It follows from our model that this entropy S^0 should be defined as

$$S^0 \equiv N_{Av}(S_H + k \ln Z_H) \ . \tag{59}$$

Then combination of Eqs (*44*) and (*54*) with our value of H^0 yields

$$S^0 = (-27\ 000 + 13\ 380)/T \ . \tag{60}$$

At 298 K, we have $S^0 = -45.6$ J/K mol, a rather high negative value. According to Eq. (*59*), S^0 consists of two contributions. The latter one, describing the effect of conformational partition function changes, can be estimated from the coordination number of the lattice and from the effective number of orientations available to a pair of successive elements of the association chain. It turns out to be slightly negative. Evidently, the dominant part of S^0 is $N_{Av}S_H$, which reflects the proper interaction of the OH group proton with the oxygen electron pair.

CONCLUSIONS

1. The method of light scattering was shown to be capable of yielding valuable thermodynamic data for mixtures of alkanols with aromatic hydrocarbons.

2. ΔG_{mix} as a function of the composition of the mixture was measured for eleven selected binary mixtures that used five alkanols and four aromatic hydrocarbons.

3. A detailed analysis was presented for a model of alcohols that form in the liquid linear chains of molecules connected by hydrogen bonds. The distribution of chain lengths is governed by rules of the thermodynamics of chemical reactions. The distribution changes when the alcohol is diluted with a nonaggregating diluent. The model considers also the contact interactions.

4. The model predicted that the equilibrium constant governing the hydrogen bonding would depend on the chain length of the alcohol if expressed in volume fractions.

5. The present experimental data as well as literature data for enthalpies of mixing conformed to the model exceedingly well.

6. The formation of hydrogen bonds was successfully described by using just two adjustable values: $G^0 = (-13\ 380 + RT \ln r_A)$ J/mol, where r_A is the number of atomic groups in the alcohol; and $H^0 = -27\ 000$ J/mol.

7. Contact interaction coefficients reflected a specific interaction between the aromatic ring and oxygen atoms in the alcohol. The enthalpic portion of the interaction was very small for the shorter alcohols and regularly increased with the size of the aliphatic portion of the alcohol. The interaction lowered the entropy due to the partial loss of the orientational freedom of the aromatic molecules interacting with the oxygen atom.

REFERENCES

1. Abdel-Azim A.-A. A., Munk P.: *J. Phys. Chem.* **1987**, *91*, 3910.
2. Abdel-Azim A.-A. A., Cheng W., El-Hibri M. J., Munk P.: *J. Phys. Chem.* **1988**, *92*, 2663.
3. Cheng W., Abdel-Azim A.-A. A., El-Hibri M. J., Du Q., Munk P.: *J. Phys. Chem.* **1989**, *93*, 8248.
4. Qin A., Abdel-Azim A-A. A., Cheng W., Munk P.: *Thermochim. Acta* **1991**, *181, 237*.
5. Munk P., Qin A., Abdel-Azim A.-A. A.: *J. Phys. Chem.* **1994**, *98*, 2694.
6. Cabannes J.: *La Diffusion Moléculaire de la Lumiere*, p. 221. Les Presses Univ. de France, Paris 1929.
7. Eykman J. F.: *Rec. Trav. Chim. Pays-Bas* **1895**, 14, 185.
8. Abdel-Azim A.-A. A, Huglin M. B: *Polymer* **1984**, *25*, 803.
9. Einstein A.: *Ann. Phys. (Leipzig)* **1910**, *33*, 1275.
10. Mrazek R. V., Van Ness H. C.: *AIChE J.* **1961**, *7*, 190.
11. Munk P., Qin A., Hoffman D. E.: *Collect. Czech. Chem. Commun.* **1993**, *58*, 2612.
12. Renon H., Prausnitz J. M.: *Chem. Eng. Sci.* **l967**, *22*, 299.
13. Kehiaian H., Treszczanowicz A.: *Bull. Soc. Chim. Fr.* **1969**, *5*, 1561.
14. Costas M., Patterson D.: *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 635.

15. Andreoli-Ball L., Patterson D., Costas M., Cáceres-Alonso M.: *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3991.
16. Pouchlý J.: *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1605.
17. Qin A., Hoffman D. E., Munk P.: *J. Chem. Eng. Data* **1992**, *37*, 66.

Petr Munk is an alumnus of the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences in Prague where he obtained the Ph.D. and DrSc. degrees. There, he specialized in a rarely used physical chemical technique – flow birefringence of macromolecular solutions. This expertise brought him in 1968 to Research Triangle Institute in North Carolina, then in 1969 to The University of Texas at Austin. There he raised in ranks to the position of Full Professor. Since 1998 he is Professor Emeritus. At the Department of Chemistry he introduced into the curriculum undergraduate and graduate courses in Polymer Chemistry. He also taught courses in Physical Chemistry. For his research he obtained grants from National Science Foundation, NASA, Army Research Office, NATO, Texas Advanced Research Program, and Welch Foundation. During the years in Texas he kept in touch with his old institute in Prague, first under the name of his Texas colleagues, after 1989 in open. Together with his Prague colleagues he obtained research grants from NATO and U.S.-Czech Grant Agency. This research led to about twenty-five publications with Czech- U.S. co-authorship.

During his years in Texas his research interests broadened. They included most techniques for polymer characterization: sedimentation analysis, light scattering, viscometry, inverse gas chromatography. He was especially interested in multimolecular particles: aggregating polymers, multienzyme complexes, block copolymer micelles. Thermodynamics of mixtures in general and polymer solutions in particular were also his favorite research topics. He is the author of a textbook "Introduction to Macromolecular Science", nine invited chapters in scientific monographs, and more than 135 refereed papers in leading scientific journals. He was one of the organizers of the NATO Advanced Scientific Institute "Solvents and Self-Organization of Polymers" held in Turkey in 1995, and a co-editor of the proceedings with the same name. He is a member of the governing board of ISPAC (International Symposia on Polymer Analysis and Characterization) that organizes yearly well-reputed symposia in different parts of the world. During his career, Petr Munk held visiting professorships at the University of Mainz in Germany, at Charles University in Prague, and Raman professorship at Madras University in India.