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Viscosimetric Study of Multicomponent Liquid Mixtures Containing Oxygenated Compounds

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Viscosities for the ternary mixtures, 1,4-dioxane + 1-butanol + cyclohexane and 1,4-dioxane + 2-butanol + cyclohexane, were determined at temperatures of 298.15 and 313.15 K. From these data the viscosity deviations were calculated and they are negative over the whole composition range. The results have been compared to predictions by the group contribution method proposed by Wu.

KEY WORDS: 1-butanol; 2-butanol; cyclohexane; 1,4-dioxane; viscosity; Wu method.

1. INTRODUCTION

Although there are a considerable number of viscosity studies of binary mixtures, references for ternary or higher-order mixtures are scarce. These studies on multicomponent mixtures can be used in engineering calculations where fluid flow is an important factor.

The present paper continues our work about transport properties of ternary mixtures involving ethers and alkanols [1–3]. We present here viscosity measurements of two ternary mixtures: 1,4-dioxane + 1-butanol + cyclohexane and 1,4-dioxane + 2-butanol + cyclohexane at 298.15 and 313.15 K. From these viscosity measurements viscosity deviations are calculated and the viscosity behavior of these mixtures are compared with that of mixtures containing 1,3-dioxolane.

The experimental results were used to test the prediction capability of the Wu- UNIFAC [4, 5] viscosity group contribution methods.

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2. EXPERIMENTAL

The compounds employed were 1,4-dioxane and cyclohexane (purities better than 99.9 mol%), 1-butanol (purity better than 99.8 mol%), and 2-butanol (purity better than 99 mol%) obtained from Aldrich. The purities of these compounds were checked by comparing measured densities with those reported in the literature and also by a chromatographic method. No further purification was considered necessary, but the 1-butanol and 2-butanol were dried with activated molecular sieve type 0.3 nm from Merck. The pure compound properties at 298.15 and 313.15 K, along with literature values at 298.15 K [6–8], are given in Table I.

Kinematic viscosities, v, were determined using an Ubbelohde viscosimeter with a Schoot–Geräte automatic measuring unit Model AVS-440. The temperature was kept constant within ±0.01 K by means of a Schoot–Geräte thermostat. The viscosimeter was calibrated with deionized doubly-distilled water. The uncertainty of the time flow measurements was ±0.01 s, and the corresponding uncertainty in the kinematic viscosity was $\pm 1 \times 10^{-4}\,\text{mm}^2 \cdot \text{hs}^{-1}$. Kinetic energy corrections were applied to the experimental data.

Densities, ρ, required for converting kinematic viscosities to absolute or dynamic viscosities ($\eta = \rho v$), were measured using an Anton Paar DMA-58 vibrating tube densimeter in which the temperature is controlled automatically within ±0.01 K. The apparatus was calibrated with deionized twice-distilled water and dry air. The precision of the density measurements is $\pm 5 \times 10^{-6}\,\text{g} \cdot \text{cm}^{-3}$, and the uncertainty of these measurements after proper calibration is $\pm 10^{-5}\,\text{g} \cdot \text{cm}^{-3}$.

Table I. Densities, ρ, and Viscosities, η, of the Pure Compounds at 298.15 and 313.15 K and Comparisons with Literature Data at 298.15 K

	T = 298.15 K				T = 313.15 K	
	ρ (g·cm^{-3})		η (mPa·s)		ρ (g·cm^{-3})	η (mPa·s)
Compound	Expt.	Lit.	Expt.	Lit.	Expt.	Expt.
1,4-Dioxane	1.02797	1.02797[a]	1.1795	1.181[c]	1.01086	0.9330
1-Butanol	0.80564	0.80575[b]	2.5458	2.5647[b]	0.79416	1.7583
2-Butanol	0.80220	0.80241[b]	3.0427	2.998[b]	0.78956	1.7913
Cyclohexane	0.77384	0.77389[b]	0.8887	0.898[b]	0.75948	0.7007

[a] Ref. 6.
[b] Ref. 7.
[c] Ref. 8.

The mixtures were prepared using a Mettler H20T balance. The maximum estimated error in the mole fractions is $\pm 1 \times 10^{-4}$.

3. RESULTS AND DISCUSSION

The viscosities of the ternary mixtures at both temperatures 298.15 and 313.15 K are given in Table II. Viscosity deviations were calculated from our measurements according to the following equation:

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2 + x_3\eta_3) \tag{1}$$

where η is the viscosity of the mixture and x_i and η_i are, respectively, the mole fraction and viscosity of component i. The values of viscosity deviations are also reported in Table II.

The viscosity deviations were correlated by means of the Redlich–Kister equation for ternary mixtures [9, 10]:

$$\Delta\eta = \Delta\eta_{\mathrm{bin}} + x_1x_2(1 - x_1 - x_2)\,(C + D_1x_1 + D_2x_2) \tag{2}$$

where

$$\begin{aligned}\Delta\eta_{\mathrm{bin}} &= x_1x_2\sum_{p=0}^{r} A_{p,12}(x_1 - x_2)^p \\ &+ x_1x_3\sum_{p=0}^{r} A_{p,13}(x_1 - x_3)^p \\ &+ x_2x_3\sum_{p=0}^{r} A_{p,23}(x_2 - x_3)^p \end{aligned} \tag{3}$$

with x_i the mole fraction of component i for a ternary mixture data point.

Table III gives the parameters, $A_{p,ij}$, for the constituent binary mixtures obtained either from experimental measurements carried out in our laboratory or taken from previous papers [1, 2]; the corresponding standard deviations, σ, are also tabulated.

The C and D_i parameters of the Redlich–Kister equation for the ternary mixtures obtained by a least-squares method, along with the standard deviations, are given in Table IV. Isolines at constant values of $\Delta\eta$, calculated from Eq. (2), have been plotted in Figs. 1 and 2.

The viscosity deviations of the two ternary systems are negative over the whole composition range at 298.15 and 313.15 K. An increase of the temperature leads to a considerable decrease of $\Delta\eta$, but the shape does not change appreciably with temperature. This behavior,

Table II. Experimental Viscosities, η, and Viscosity Deviations, $\Delta\eta$, of the Ternary Mixtures

		$T = 298.15\,\mathrm{K}$		$T = 313.15\,\mathrm{K}$	
x_1	x_2	η (mPa·s)	$\Delta\eta$ (mPa·s)	η (mPa·s)	$\Delta\eta$ (mPa·s)
		1,4-Dioxane (1) + 1-butanol (2) + cyclohexane (3)			
0.1028	0.8184	1.7414	−0.5386	1.2692	−0.3284
0.1037	0.7329	1.5535	−0.5845	1.1442	−0.3623
0.1028	0.6412	1.3924	−0.5927	1.0354	−0.3731
0.1014	0.5433	1.2287	−0.5933	0.9258	−0.3780
0.1022	0.4433	1.0972	−0.5586	0.8394	−0.3579
0.1059	0.3141	0.9700	−0.4719	0.7551	−0.3052
0.1014	0.2175	0.9186	−0.3613	0.7150	−0.2413
0.1017	0.0926	0.8546	−0.2177	0.6756	−0.1475
0.1465	0.7509	1.5451	−0.6353	1.1446	−0.3911
0.2021	0.6010	1.2567	−0.6905	0.9552	−0.4335
0.2043	0.4993	1.1235	−0.6551	0.8646	−0.4161
0.2075	0.3884	1.0098	−0.5853	0.7870	−0.3762
0.2020	0.2990	0.9404	−0.5044	0.7384	−0.3281
0.2059	0.1932	0.8593	−0.4106	0.6803	−0.2743
0.2016	0.0987	0.8232	−0.2883	0.6553	−0.1975
0.3046	0.5998	1.2103	−0.7647	0.9298	−0.4815
0.3053	0.4975	1.0881	−0.7169	0.8441	−0.4582
0.3052	0.3977	0.9913	−0.6477	0.7768	−0.4190
0.3030	0.2979	0.9182	−0.5541	0.7249	−0.3639
0.3049	0.1935	0.8601	−0.4391	0.6833	−0.2946
0.3052	0.0951	0.8236	−0.3120	0.6578	−0.2152
0.4080	0.4954	1.1045	−0.7269	0.8596	−0.4643
0.4044	0.3974	1.0050	−0.6624	0.7898	−0.4287
0.4046	0.2975	0.9345	−0.5667	0.7426	−0.3695
0.4115	0.1848	0.8706	−0.4451	0.6941	−0.2993
0.4026	0.0976	0.8402	−0.3279	0.6700	−0.2283
0.5065	0.3979	1.0381	−0.6597	0.8170	−0.4258
0.5169	0.2893	0.9595	−0.5607	0.7596	−0.3697
0.5064	0.1954	0.8996	−0.4614	0.7179	−0.3089
0.5040	0.0958	0.8606	−0.3340	0.6897	−0.2302
0.6071	0.2943	0.9989	−0.5560	0.7932	−0.3624
0.6072	0.1956	0.9375	−0.4532	0.7491	−0.3013
0.6035	0.0984	0.8955	−0.3324	0.7173	−0.2285
0.7062	0.1970	0.9858	−0.4360	0.7900	−0.2489
0.7067	0.0961	0.9438	−0.3102	0.7555	0.2118
0.8079	0.0955	1.0184	−0.2641	0.8050	−0.1852
0.0527	0.8996	2.002	−0.4002	1.4263	−0.2463
0.0505	0.8439	1.8594	−0.4477	1.3335	−0.2793
0.0512	0.0949	0.8500	−0.2114	0.6694	−0.1443
0.0505	0.0459	0.8381	−0.1416	0.6626	−0.0988
0.1031	0.8512	1.7748	−0.5597	1.2908	−0.3418
0.1009	0.0450	0.8246	−0.1682	0.6540	−0.1181

Table II. *(Continued)*

		$T = 298.15\,\mathrm{K}$		$T = 313.15\,\mathrm{K}$	
x_1	x_2	η (mPa·s)	$\Delta\eta$ (mPa·s)	η (mPa·s)	$\Delta\eta$ (mPa·s)
1,4-Dioxane (1) + 1-butanol (2) + cyclohexane (3)					
0.8578	0.0948	1.0474	−0.2485	0.8444	−0.1566
0.8566	0.0454	1.0280	−0.1853	0.8199	−0.1282
0.9084	0.0446	1.0726	−0.1545	0.8552	−0.1041
1,4-Dioxane (2) + 2-butanol (2) + cyclohexane (3)					
0.0539	0.8990	2.1387	−0.7021	1.3731	−0.3206
0.1002	0.8516	1.8346	−0.9176	1.2284	−0.4243
0.8525	0.0989	1.0611	−0.2885	0.8489	−0.1577
0.9036	0.0483	1.0897	−0.1658	0.8660	−0.0973
0.0502	0.8516	1.9316	−0.8060	1.2618	−0.3793
0.1011	0.8006	1.6609	−0.9817	1.1333	−0.4640
0.2018	0.7011	1.3443	−1.1133	0.9680	−0.5442
0.2995	0.6051	1.1815	−1.0977	0.8788	−0.5514
0.4041	0.4973	1.0691	−1.0083	0.8181	−0.5188
0.5036	0.4004	1.0261	−0.8715	0.8078	−0.4466
0.6004	0.3015	0.9914	−0.7213	0.7797	−0.3893
0.7001	0.2017	0.9930	−0.5338	0.7860	−0.2973
0.8027	0.0987	1.0189	−0.3158	0.8108	−0.1840
0.8520	0.0486	1.0457	−0.1954	0.8309	−0.1207
0.0996	0.7032	1.3987	−1.0337	0.9937	−0.4970
0.2001	0.6027	1.1738	−1.0713	0.8662	−0.5383
0.3019	0.5021	1.0483	−1.0097	0.8008	−0.5176
0.4031	0.3998	0.9775	−0.8896	0.7597	−0.4707
0.5041	0.2994	0.9452	−0.7350	0.7432	−0.4011
0.6046	0.1995	0.9363	−0.5579	0.7438	−0.3149
0.7048	0.0985	0.9541	−0.3517	0.7613	−0.2105
0.1112	0.5960	1.1904	−1.0144	0.8650	−0.5115
0.2030	0.5013	1.0440	−0.9835	0.7883	−0.5063
0.3019	0.4028	0.9591	−0.8850	0.7418	−0.4683
0.4021	0.3026	0.9137	−0.7437	0.7179	−0.4062
0.5190	0.1941	0.9001	−0.5576	0.7140	−0.3189
0.6041	0.1010	0.9053	−0.3766	0.7226	−0.2286
0.1004	0.5032	1.0659	−0.9359	0.7932	−0.4796
0.2031	0.4028	0.9550	−0.8604	0.7340	−0.4532
0.3007	0.3077	0.8995	−0.7394	0.7032	−0.4029
0.4028	0.2019	0.8687	−0.5720	0.6885	−0.3260
0.5026	0.1000	0.8679	−0.3824	0.6941	−0.2324
0.1009	0.4024	0.9688	−0.8160	0.7365	−0.4265
0.2036	0.2982	0.8905	−0.6997	0.6932	−0.3800
0.2942	0.1978	0.8510	−0.5493	0.6820	−0.3028
0.3979	0.1015	0.8446	−0.3784	0.6748	−0.2290
0.1021	0.3034	0.9113	−0.6606	0.7009	−0.3544
0.2064	0.1973	0.8481	−0.5256	0.6677	−0.2961
0.3054	0.1005	0.8285	−0.3655	0.6596	−0.2216

Table II. *(Continued)*

		$T = 298.15\,\mathrm{K}$		$T = 313.15\,\mathrm{K}$	
x_1	x_2	η (mPa·s)	$\Delta\eta$ (mPa·s)	η (mPa·s)	$\Delta\eta$ (mPa·s)
0.1007	0.1959	0.8588	−0.4812	0.6710	−0.2667
0.2091	0.0994	0.8248	−0.3388	0.6580	−0.1997
0.1031	0.0974	0.8378	−0.2907	0.6606	−0.1703
0.0494	0.1025	0.8517	−0.2722	0.6673	−0.1567
0.1017	0.0651	0.8342	−0.2243	0.6593	−0.1360
0.0493	0.0499	0.8486	−0.1619	0.6678	−0.0988

Table III. Parameters of the Redlich–Kister Equation, A_p, for the Constituent Binary Mixtures and Standard Deviations, $\sigma(\Delta\eta)$

System	T (K)	A_0	A_1	A_2	A_3	$\sigma(\Delta\eta)$
1,4-Dioxane (1) +	298.15	−2.7891	1.3432	−1.3829	0.8008	0.0076
1-butanol (2)	313.15	−1.7618	0.7661	−0.7640	0.3770	0.0025
1,4-Dioxane (1) +	298.15	−0.6703	−0.0280	−0.1672	0.0500	0.0004
cyclohexane (3)	313.15	−0.4933	0.0085	−0.1064	−0.0224	0.0025
1-Butanol (2) +	298.15	−1.7492	0.1349	0.0405	−0.1273	0.0030
cyclohexane (3)[a]	313.15	−1.1670	0.0180	−0.0164	−0.0067	0.0027
1,4-Dioxane (1) +	298.15	−3.9470	2.3848	−2.9638	2.2011	0.0230
2-butanol (2)	313.15	−2.0054	0.9988	−1.2228	0.8458	0.0097
2-Butanol (2) +	298.15	−3.3774	−1.5283	−0.9126	−0.4790	0.0056
cyclohexane (3)[b]	313.15	−1.7343	−0.7336	−0.4360	−0.0809	0.0026

[a] Ref. 1.

[b] Ref. 2.

Table IV. Parameters of the Redlich–Kister Equation for the Ternary Mixtures, C and D_i, and Standard Deviations, $\sigma(\Delta\eta)$

System	T (K)	C	D_1	D_2	$\sigma(\Delta\eta)$
(1) + 1-butanol (2) +	298.15	1.0546	−2.0511	−3.1409	0.0139
cyclohexane (3)	313.15	0.6893	−1.8950	−1.1882	0.0090
1,4-Dioxane (1) + 2-butanol (2)+	298.15	1.1818	−0.1577	5.6608	0.0029
cyclohexane (3)	313.15	0.5398	−0.2614	2.7132	0.0010

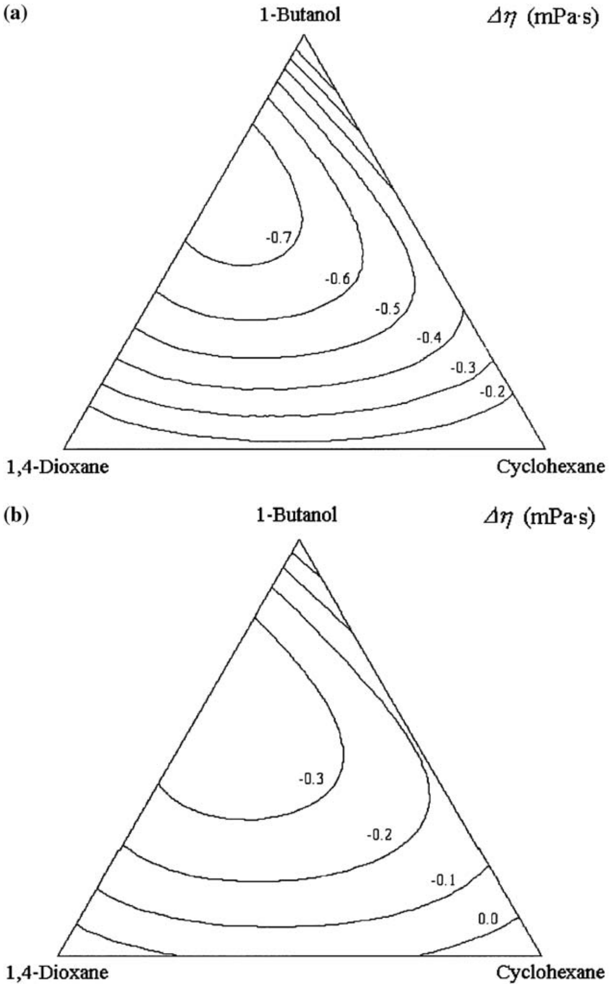

Fig. 1. Isolines of constant viscosity deviation, $\Delta\eta$, of the ternary system 1,4-dioxane (1) + 1-butanol (2) + cylohexane (3): (a) at 298.15 K and (b) at 313.15 K.

i.e., negative values of $\Delta\eta$, is expected in mixtures in which the predominant effects, during the mixing process, involve weakening of the interactions between the pure components [11], in our case dipole–dipole interactions in 1,4-dioxane and hydrogen-bonding in 1-butanol and 2-butanol.

It can also be observed that the viscosity deviations for the mixture containing 2-butanol are much larger than for the mixture containing the

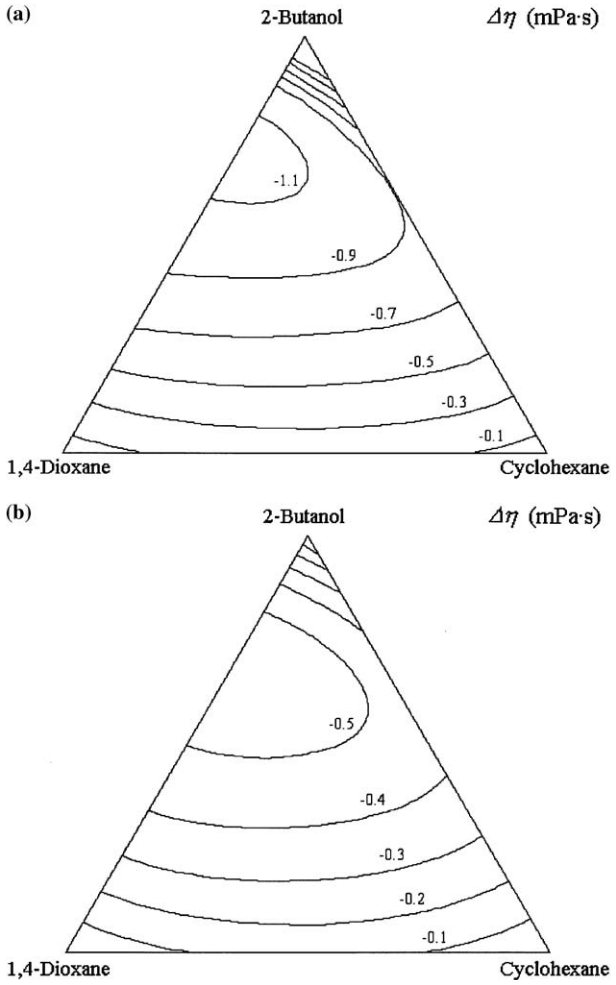

Fig. 2. Isolines of constant viscosity deviation, $\Delta\eta$, of the ternary system 1,4-dioxane (1) + 2-butanol (2) + cylohexane (3): (a) at 298.15 K and (b) at 313.15 K.

primary butanol. This is due to the fact that the hydrogen-bond structure of 2-butanol is broken to a greater extent in the mixing process [12] leading to a less viscous mixture.

Finally, if we compare the viscosity behavior for the ternary mixtures containing 1,3-dioxolane or 1,4-dioxane we can see that $\Delta\eta$ values are very similar, showing that for these kinds of mixtures the viscosity behavior is principally influenced by the isomeric butanol.

Table V. Viscosity Predictions for the Ternary Mixtures

System	T (K)	MRSD (%) $A=1$	MRSD (%) $A=2.45$
1,4-Dioxane (1) + 1-butanol (2) + cyclohexane (3)	298.15	11.1	16.5
	313.15	10.4	14.4
1,4-Dioxane (1) + 2-butanol (2) + cyclohexane (3)	298.15	12.5	28.6
	313.15	9.6	20.3

4. VISCOSITY PREDICTIONS

The Wu model [4] was used to predict the viscosities of the systems. This model is based on the following modified Eyring viscosity equation [13]:

$$\eta = \frac{hN}{V} \exp\left[\frac{(x_i G_i^*) - \frac{G^{\mathrm{E}}}{A}}{RT}\right] \tag{4}$$

where h is Planck's constant, N is Avogadro's number, V is the molar volume of the liquid mixture, x_i and G_i^* are the mole fraction and the Gibbs energy of activation for viscous flow of component i, respectively, G^{E} is the Gibbs excess energy of the liquid mixture at the corresponding mole fraction, A is an empirical factor (A=1 or A=2.45), T is the temperature, and R is the universal gas constant. G_i^* can be obtained from the corresponding viscosity and molar volume of the pure compound [4]. G^{E} can be estimated by using a group contribution model; here we have employed the UNIFAC method.

For all the systems the viscosities obtained experimentally were compared with the viscosity predictions and the mean relative standard deviations (*MRSD*) are given in Table V. These values indicate that the Wu-UNIFAC method with $A=1$ provides rather good predictions of viscosity values at the two temperatures; in this case, the overall *MRSD* average is 10.9%.

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REFERENCES

1. I. Gascón, M. C. López, M. M. Domínguez, F. M. Royo, and J. S. Urieta, *J. Chem. Eng. Jpn.* **33**:740 (2000).

2. I. Gascón, A. M. Mainar, F. M. Royo, J. S. Urieta, and L. Alvarez-Cerdeiriña, *J. Chem. Eng. Data* **45**:751 (2000).
3. I. Gascón, J. Pardo, J. Santafé, M. Domínguez, and J. S. Urieta, *Fluid Phase Equilibr*. **180**:211 (2001).
4. D. T. Wu, *Fluid Phase Equilibr.* **30**:146 (1986).
5. J. Gmehling, J. Li, and M. Schiler, *Ind. Eng. Chem. Res*. **32**:178 (1993).
6. P. Brocos, E. Calvo, A. Amigo, R. Bravo, M. Pinto, A.H. Roux, and G. Roux-Desgranges, *J. Chem. Eng. Data* **43**:112 (1998).
7. J. A. Riddick, N. B. Bunger, and T. K. Sakano. *Organic Solvents, Physical Properties and Methods of Purification (Techniques of Chemistry)*, 4th Ed. (Wiley Interscience, New York, 1986).
8. I. L. Acevedo, G. C. Pedrosa, and M. Katz, *Can. J. Chem.* **69**:1006 (1991).
9. O. Redlich and A. T. Kister, *Ind. Eng. Chem.* **40**:345 (1948).
10. I. Cibulka, *Coll. Czech. Commun.* **47**:1414 (1982).
11. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.* **62**:1112 (1966).
12. I. Gascón, H. Artigas, S. Martín, P. Cea, and C. Lafuente, *J. Chem. Thermodyn*. **34**:1351 (2002).
13. R. E. Powell, W. E. Roseveare, and H. Eyring, *Indust. Eng. Chem.* **33**:430 (1941).